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# THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at Burlington House, London, W.1, on 20 October 1954, the Chair being taken by the President, Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.

**The General Secretary** read the minutes of the previous meeting, which were confirmed and signed as a correct record. He then announced the names of members elected since the previous meeting, and gave notice of the date of the next meeting.

**The President,** introducing the author of the paper to be presented, said: It gives me much pleasure to be in the Chair tonight, and to present our ever popular speaker, Dr Gustav Egloff. To introduce him would be work of supererogation, for there is nobody I know in the profession of petroleum technology who has gained more respect and popularity and is so well known in all parts of the world. He is truly a man of dynamic personality. His energy seems unbounded, and I can well understand his winning wrestling championships at Cornell prior to wrestling with his innumerable patents and papers and establishing records with them.

The history of the Institute of Petroleum seems to have been built up around Dr Egloff, and has fortunately been punctuated by his appearance in person from time to time. It is again an honour to ask him to speak—this time on the latest but certainly not the least of his interests, the Platforming process.

The following paper was then presented in summary by the author:

## THE PLATFORMING PROCESS

By GUSTAV EGLOFF,* M.A., D.Sc., Ph.D. (Fellow)

### INTRODUCTION

THE UOP Platforming process is solving three of the most important problems which confront petroleum refiners today. These are the ever-increasing octane requirements of motor gasoline, the production of aromatic hydrocarbons for chemical manufacture, and the production of hydrogen for upgrading charging stocks and for other purposes, such as the manufacture of ammonia. The UOP Platforming process has pioneered the use of platinum in a reforming catalyst. Since its first commercial operation in 1949, reforming processes using platinum in the catalyst, in conjunction with catalytic cracking, have enabled the refining industry to produce large quantities of high octane gasoline, both in the U.S.A. and elsewhere, including the British Isles, Western Europe, Australia, Japan, the Middle East, and Canada. The Unifining process, which utilizes by-product hydrogen from Platforming or other catalytic reforming processes, has been brought into commercial use more recently.

The necessity for widespread installation of this process for production of high octane gasoline is evident in the trend toward higher compression ratios in automobile engines. In the U.S.A. some 1954 model automobiles have compression ratios as high as 8·50 : 1, and no new models have less than 7·00 : 1. To meet these requirements, the average octane number of premium gasoline was running between 93 and 94 in mid-1954. During the latter half of 1955, the average is expected to reach 96 and advance still further to 97·5 in 1957 with some gasolines of 100 octane rating on the market. These qualities of fuel may be a necessity at that time in view of forecasts that automobile engines having 10 : 1 compression ratios or higher will be produced.

The demands which the refiner must meet entail not only higher octanes but larger quantities of premium fuel. Installation of UOP Platforming and other catalytic reforming processes is proceeding at an extremely rapid rate to meet these demands. Plants operating or contracted for equal about 10·7 per cent of the total crude capacity. Continued growth of 20 to 25 per cent of crude capacity is anticipated on the basis of the wider range of charging stocks that can now be used.

The importance of the Platforming process becomes greater as the octane numbers of products are increased through process improvements and experience in operation. Some operators are now operating to produce gasolines having octane numbers as high as 98 leaded.

Demands for benzene, toluene, and the xylenes as basic materials for chemical manufacture now exceed the quantities available as by-products of the coal coking industry, both in the U.S.A. and elsewhere. As a result, UOP Platforming and other catalytic processes are being used increasingly for the production of aromatic hydrocarbons. The unprecedented demands result from the increasing use of chemicals as raw materials for many products, particularly plastics, rubber, textiles, detergents, and agricultural chemicals. A continual increase in requirements can be predicted not only on the basis of population growth but on the development of many new products. A good example of newly created demands for petroleum derived aromatics through technical development is the chemical utilization of the xylenes. Previously used only in a mixture for solvents, the *ortho* component of the xylene fraction is now converted to phthalic anhydride, the *para* component to dimethyl terephthalate for Dacron or Terylene fibre

* Universal Oil Products Company, Des Plaines, Illinois, U.S.A.

and Mylar film, and the *meta* component will be utilized for commercial production of *iso*phthalic acid for consumption in plastics.

New and greatly improved separation processes are also a highly important factor in the recent development of high-purity aromatics by catalytic reforming. The Udex process, in which solvent extraction is carried out with aqueous solutions of diethylene glycol, makes possible the recovery of nitration grade benzene and toluene, and the xylenes from the gasoline fraction. Other separation processes used for this purpose include phenols and sulphur dioxide extraction and extractive distillation. High purity *o*- and *p*-xylene are recovered from the xylene fraction by subsequent fractional distillation and fractional crystallization.

The by-product hydrogen available from Platforming makes possible a number of operations which result in improved gasoline and oil products, the availability of a wider range of charging stocks, greater refinery flexibility, and the production of chemicals. The amount of hydrogen available varies from about 300 to 1500 cu. ft/brl of charge. Currently production averages 500 to 600 cu. ft/brl. One application is in the manufacture of synthetic ammonia. A more widespread use is in the catalytic hydrogenation of charging stock for other refinery processes.

One of the most widely used of these processes is Unifining, in which hydrogenation is carried out over catalysts containing cobalt and molybdenum compounds. This operation results in almost complete removal of sulphur, nitrogen, and metals, the saturation of olefins, and decomposition of oxygen compounds with little or no loss in volume. One of the principal applications is the pretreating of Platforming charge stocks; thus a wider variety of stocks are rendered suitable for Platforming. These include straight-run naphthas of abnormally high sulphur, nitrogen or metals content, thermally cracked gasoline, and coker gasolines. Another application of Unifining naphthas is in the production of premium quality solvent naphthas. The process is also used for both virgin and cracked middle distillates to produce premium quality diesel fuels, stove oils, and kerosines. Likewise, Unifining upgrades heavy distillates to high quality fuel oils. Successful operation with heavy distillates is also important in that low quality gas oils can be improved for use as catalytic cracking stock. Unifining is also applicable to the processing of distillates from the coking of coal and of raw bitumen from tar sands and from crude shale oils. The tar sand distillates composed of about 50 per cent sulphur-containing compounds are converted into a product equivalent to a corresponding mixed cut from sweet crude oil. Shale oils of unusually high nitrogen content are converted to high-grade diesel fuels.

The commercial use of Unifining and Udex processes followed commercial installation of the Platforming process. They serve as outstanding examples of the continuously broadening scope of Platforming in petroleum refining.

## PROCESS DESCRIPTION

In the UOP Platforming process a catalyst is employed which contains platinum. This catalyst has high efficiency, high activity, and low carbon-forming tendency. The process is non-regenerative, and thus avoids the use of costly and complex equipment inherent in regeneration. Commercial operations average over 96 per cent on-stream time. The low carbon-forming tendency of the catalyst assures the maintenance of high catalyst activity over a long period of time. Catalyst life of over 70 brl of reformed gasoline/1 lb of catalyst are average. One commercial unit was in continuous operation for almost two years and reached a yield of over 250 brl of naphtha/1 lb of catalyst.

The process flow in a typical Platforming unit is indicated diagrammatically in Fig 1. The charge is heated and passed along with recycle hydrogen through a combined feed heater and through a series

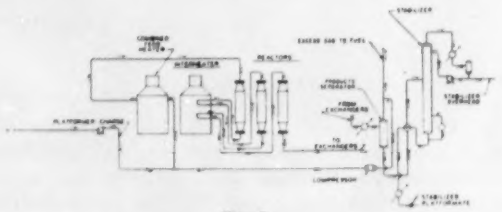


Fig 1
FLOW DIAGRAM OF PLATFORMER UNIT

of reactors containing stationary beds of Platforming catalyst. Provision is made for heating the stream of products between the reactors to maintain reaction temperature. The overall reactions in Platforming are endothermic, because dehydrogenation of naphthenes to aromatics is one of the predominant reactions, even though exothermic hydrogenation reactions partly counteract the endothermic effects. After cooling by passage through heat exchangers the products are separated into gas and liquid, and the liquid products are stabilized to the desired vapour pressure.

The hydrogen from the Platforming unit is recycled to maintain the necessary molal excess in the reaction zone. It is characteristic of Platforming that the recycle gas contains 80 to 95 per cent hydrogen, since only small amounts of normally gaseous hydrocarbons, such as methane, ethane, and propane, are produced. In some cases, after products from the Platformer have been cooled, the separated gas is passed through a purifying column to remove hydrogen sulphide.

Operating conditions vary with charging stocks used and end-products desired. When Platforming gasoline or naphtha for octane number improvement, temperatures are usually between 850° and 950° F (455° and 510° C) and pressures from 300 to 900 p.s.i.g. Relatively higher temperatures and lower pressures are used in the production of aromatics.

Table I contains experimental data showing the effect of temperature on the Platforming reaction. As the temperature increased from 813° to 903° F (435° to 485° C) the F-1 octane number increased from 67·5 to 89 clear, and 85 to 98·5 with 3 ml TEL, while the yield of Platformate decreased from 98 to 91·6 per cent. The percentage of aromatics in the product increased from 19 to 45 with this rise in temperature. The hydrogen produced increased from 166 cu. ft/brl to 466 cu. ft. with increased temperature.

The effect of decreasing the operating pressure is shown in Table II. In going from 900 to 500 lb the yield of aromatics based on the charge increased from 45·4 to 53·9 per cent, along with a marked rise in hydrogen production from 287 to 685 cu. ft/brl. Decreasing the pressure also decreased the volatility of the product, as shown by the percentage over at 212° F (100° C). In general, yields increase with decreased pressure.

TABLE I

*Effect of Temperature on Platformate*

| | Charge * | | | | |
|---|---|---|---|---|---|
| Average catalyst temp, ° F | — | 813 | 843 | 873 | 903 |
| Yield of $C_5$+, liquid vol % of charge | 100·0 | 98·0 | 96·8 | 95·0 | 91·6 |
| Vapour pressure at 100° F | 5·5 | 6·0 | 6·7 | 8·3 | 11·4 |
| F-1 clear octane no. | 61·0 | 67·5 | 74·0 | 80·5 | 89·0 |
| F-1 + 3 ml TEL | 80·2 | 85 | 88 | 92·5 | 98·5 |
| Aromatics in product, % | 9 | 19 | 27 | 35 | 45 |
| Over at 212° F, % | 31 | 34 | 36 | 41 | 46 |
| Hydrogen production, cu. ft/brl | — | 166 | 318 | 420 | 466 |

* I.B.P. to 350° F Mid-Continent naphtha.

TABLE II

*Effect of Operating Pressure on Platformate*

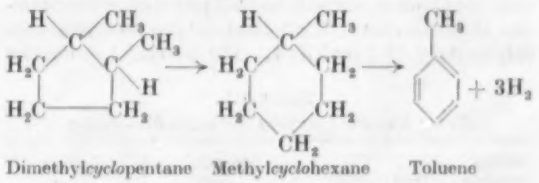
| | Charge * | Products | | |
|---|---|---|---|---|
| Pressure, p.s.i.g. | — | 900 | 700 | 500 |
| Yield, vol % of charge : | | | | |
| 10 lb RVP Platformate | — | 92·4† | 96·4‡ | 97·3§ |
| F-1 clear octane no. | 35·0 | 84·8 | 83·2 | 84·2 |
| F-1 + 3 ml TEL | 52·8 | 94·9 | 94·3 | 95·2 |
| Aromatics based on charge, % | 7·1 | 45·4 | 47·9 | 53·9 |
| Over at 212° F + loss, % | 0 | 22·7 | 18·9 | 12·7 |
| Hydrogen production, cu. ft/brl | — | 287 | 488 | 686 |

* 247° to 404° F Mid-Continent, straight-run naphtha.
† Slight excess butane produced.
‡ With 3·5% outside butane.
§ With 4·7% outside butane.

## REACTIONS

The reactions occurring in Platforming involve: (1) isomerization of naphthenes, (2) dehydrogenation of naphthenes, (3) dehydrocyclization of paraffins, (4) hydrocracking, (5) isomerization of paraffins, and (6) desulphurization. These reactions are more or less simultaneous and concurrent and take place to varying extents, depending upon the composition of the stock being Platformed and the severity of operating conditions. It is therefore difficult to isolate any one reaction, particularly isomerization, which accompanies many of the other conversion reactions.

The Platforming catalyst is particularly effective in dehydrogenating *cyclo*hexane and its alkyl derivatives. The catalyst also effects isomerization of methyl and other alkyl *cyclo*pentanes to *cyclo*hexanes, which are then dehydrogenated to corresponding aromatics.

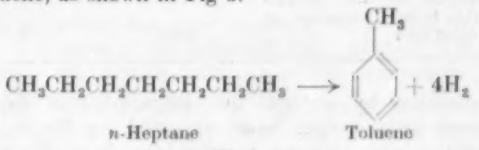


Dimethyl*cyclo*pentane Methyl*cyclo*hexane Toluene

FIG 2

The equations given in Fig 2 are typical of the conversion of methyl*cyclo*pentanes to aromatics. A dimethyl*cyclo*pentane may be first isomerized to methyl*cyclo*hexane, which is in turn dehydrogenated to toluene.

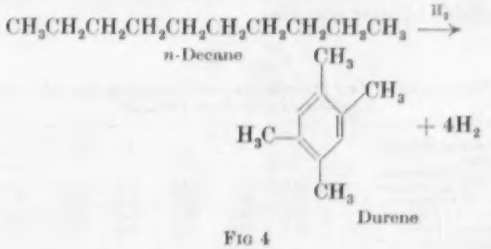
The dehydrocyclization reaction also occurs in Platforming to convert some paraffins to aromatics. A simple example is the conversion of *n*-heptane to toluene, as shown in Fig 3.



*n*-Heptane Toluene

FIG 3

Fig 4 shows a typical conversion of *n*-decane to a tetramethylbenzene by dehydrocyclization.



*n*-Decane Durene

FIG 4

The amount of dehydrocyclization of paraffin hydrocarbons to produce aromatics has been found to undergo wide variations, depending upon the hydrocarbon composition of the charging stock and the intensity of operating conditions. When a predominantly naphthenic charge is processed, aromatics production can be attributed principally to dehydrogenation and isomerization of naphthenes, while in the case of a highly paraffinic charge, dehydrocyclization reactions play an important role in the production of aromatics. In the latter case the dehydrocyclization reactions are fostered by conditions of relatively high severity.

To show the amount of dehydrocyclization taking place with essentially different charging stocks and under different operating conditions, two heavy naphthas were Platformed under conditions of varying

severity. The stocks processed were a low paraffin-content naphtha from a Venezuela crude oil and a high paraffin content naphtha from a Kuwait crude oil. Their compositions and properties are shown in Table III. The Venezuela stock contained 39·4 per cent paraffins in contrast to 66·3 per cent in the naphtha from Kuwait. Their clear octane numbers were respectively 52·2 and 32·4. The potential aromatics

TABLE III

*Heavy Naphtha Charging Stocks for Platforming*

| Source | Venezuela Low | | Kuwait High | |
|---|---|---|---|---|
| Paraffin content | | | | |
| Composition : | vol % | wt % | vol % | wt % |
| Paraffins | 39·4 | 36·5 | 66·3 | 63·3 |
| Naphthenes | 39·5 | 40·1 | 19·8 | 20·8 |
| Aromatics | 21·1 | 23·4 | 13·9 | 15·9 |
| Properties : | | | | |
| F-1 clear octane no. | 52·2 | | 32·4 | |
| F-1 + 3 ml TEL | 73·6 | | 55·2 | |
| Engler distillation, ° F : | | | | |
| I.B.P. | 272 | | 272 | |
| E.P. | 374 | | 378 | |
| Potential aromatic production from aromatics and naphthenes, wt % of feed | 61·6 | | 35·7 | |
| Potential aromatic production from naphthenes, wt % of feed | 38·2 | | 19·8 | |

production by straight dehydrogenation of naphthenes on a weight basis was 38·2 for Venezuela naphtha and 19·8 for the naphtha from Kuwait. Each of the two charge stocks was processed in a series of runs of increasing severity at different pressures.

When the low-paraffin Venezuela charge was processed at an intermediate pressure, the results shown in Table IV were obtained.

TABLE IV

*Platforming of Low Paraffin-content Venezuela Straight-run Naphtha Intermediate Pressure*

| Increasing severity | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Yields : | | | | | | |
| $C_5$ + Platformate, liq vol % of charge | 91·8 | 90·2 | 89·5 | 87·2 | 85·0 | 81·6 |
| F-1 clear octane no. | 86·7 | 89·1 | 90·4 | 93·3 | 96·3 | 98·4 |
| F-1 + 3 ml TEL | 94·8 | 96·4 | 97·4 | 99·0 | 99·9 | (102·1) * |
| Aromatic content, wt % | 56·7 | 61·0 | 62·4 | 66·4 | 72·0 | 75·8 |
| Engler distillation, ° F : | | | | | | |
| I.B.P. | 177 | 154 | 165 | 144 | 123 | 136 |
| E.P. | 412 | 416 | 417 | 434 | 430 | 435 |
| Total aromatic production, wt % of charge | 52·4 | 56·5 | 57·5 | 59·7 | 63·4 | 61·2 |
| Net aromatic production, wt % of charge | 30·0 | 33·1 | 34·1 | 36·3 | 40·0 | 40·8 |
| Percentage of potential production calculated from naphthene composition † | 78·5 | 86·7 | 89·2 | 93·0 | 103 | 107 |

* Blending octane number; equivalent to +0·25 ml TEL.

† $\frac{\text{Net aromatic production}}{\text{Potential production from naphthenes}} = \frac{30{\cdot}0 \text{ (Table IV)}}{38{\cdot}2 \text{ (Table III)}} = 78{\cdot}5$ per cent.

When the high paraffin Kuwait charge was processed at an intermediate pressure, the results were as shown in Table V.

In the case of the Venezuela low paraffin-content charge, dehydrocyclization of paraffins played a minor role in aromatics production. The aromatics production from naphthenes reached over 100 per cent of the theoretical yield from naphthenes under the most severe operating conditions.

In the runs with the high paraffin Kuwait charge the production of aromatics was over the potential yield from naphthenes in all cases. The yield of aromatics based on the potential from naphthenes varied from 142 to 157 per cent. These data give evidence that the aromatic yields of over 100 per cent were accounted for by the dehydrocyclization of paraffin hydrocarbons and that at least in the case of the higher paraffin content charge stock dehydrocyclization played a role in aromatics production in every case.

Another of the important reactions in Platforming is hydrocracking. In this reaction high-boiling paraffin hydrocarbons are split and hydrogenated by the

TABLE V

*Platforming of a High Paraffin-content Kuwait Straight-run Naphtha Intermediate Pressure*

| Increasing severity | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Yields : | | | | |
| $C_5$ + Platformates, liq vol % of charge | 85·3 | 84·1 | 81·0 | 76·6 |
| Properties of $C_5$ + Platformate : | | | | |
| F-1 clear octane no. | 83·6 | 86·2 | 91·2 | 95·2 |
| F-1 + 3 ml TEL | 95·2 | 96·2 | 99·0 | (100·9) * |
| Aromatic content, wt % | 51·0 | 51·1 | 56·4 | 59·6 |
| Engler distillation, ° F : | | | | |
| I.B.P. | 134 | 126 | 130 | 124 |
| E.P. | 406 | 410 | 424 | 414 |
| Total aromatic production, wt % of charge | 44·1 | 43·6 | 46·6 | 47·0 |
| Net aromatic production from naphthenes, wt % of charge | 28·2 | 27·7 | 30·7 | 31·1 |
| Percentage of potential production calculated from naphthene composition | 142 | 140 | 155 | 157 |

* Blending octane number, equivalent to +0·08 ml TEL.

hydrogen present in the reaction zone to form lower boiling paraffins. The hydrocracking reaction is slower than the dehydrogenation reaction, and is exothermic in character. Isomerization is concurrent with hydrocracking, so that some branched-chain, as well as straight-chain, paraffins are obtained. Thus from *n*-decane, *n*-pentane and *iso*pentane are produced (Fig 5).

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + H_2 \longrightarrow$$

*n*-Decane

$$CH_3CH_2CH_2CH_2CH_3 + CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

*n*-Pentane *iso*Pentane

FIG 5

The loss in volume in Platforming because of production of aromatics with higher specific gravity than the corresponding paraffins and naphthenes is compensated for by hydrocracking reactions which produce higher volume and lower specific gravity products. For example, in hydrocracking *n*-decane to *n*- and *iso*pentane the volume yield is 118 per cent at 100 per cent conversion, while in converting *cyclo*hexane to benzene there is a shrinkage of about 18 per cent.

To establish the occurrence of isomerization of paraffins, *n*-pentane alone was passed through a

Platforming unit. The major reaction was isomerization to *iso*pentane. A good overall picture of the isomerization reactions occurring in the hexane fraction of a gasoline during Platforming is given in Table VI. The data show that there has been a reduction in the percentage of *n*-hexane, with increases in the percentages of methylpentanes and dimethylbutanes.

TABLE VI

*Composition of a Hexane Fraction Before and After Platforming*

| Compound | Charge | Product |
|---|---|---|
| 2,2-Dimethylbutane | 0·7 | 4·9 |
| 2,3-Dimethylbutane | 2·6 | 6·0 |
| 2-Methylpentane | 19·5 | 30·2 |
| 3-Methylpentane | 19·4 | 23·1 |
| *n*-Hexane | 57·8 | 35·8 |
| | 100·0 | 100·0 |

The Platforming catalyst is extremely efficient in desulphurizing. Residual sulphur content of the product is usually between 0·002 and 0·005 per cent, depending upon the sulphur content of the charging stock and the character of the sulphur compounds. The sulphur is converted to hydrogen sulphide, which is easily removed from the gaseous products by alkaline reagents and from liquid products either by distillation or treatment with alkaline wash liquids. This is in contrast to thermal reforming, which yields mercaptans, not all of which are removable by distillation or alkali washing. The hydrogen sulphide can be used as a source of sulphur or sulphuric acid by standard conversion processes.

## GASOLINE PRODUCTION

When the Platforming process is used to raise the octane number of natural and straight-run gasolines or naphthas, the more common procedure is to process only the higher boiling portions of the gasolines, such as those boiling from 175° to 400° F (80° to 205° C), since such fractions are of low octane rating, while the fractions boiling under 175° F (80° C) usually have ratings high enough to require no improvement. In preparing naphthas for Platforming pentanes and hexanes are removed by distillation. These latter compounds have clear research octane numbers of about 74, which are raised to over 93 by the addition of 3 ml of TEL.

When applying the Platforming process to cracked naphthas which have not been subjected to Unifining or other hydrogenation processes for saturation of olefins, it is usually advantageous to process them in admixture with a straight-run or natural gasoline fraction of similar boiling range. The latter gasoline fractions contain a higher percentage of combined hydrogen, which offsets the lower content in cracked naphthas.

Platforming raises the octane numbers in the range from 30 to 50 Research to as high as from 85 to 95 leaded, with yields ranging from 95 to 85 per cent.

Some typical results are illustrated by runs using Middle East charging stocks. The properties of two Middle East charging stocks for Platforming are shown in Table VII, the data including the analysis for paraffins, naphthenes, aromatics, and olefins. The stocks were each Platformed under varying conditions of severity to obtain data on the relation between the properties of the charge materials and the quality and

TABLE VII

*Platforming of Middle East Naphthas, Charging Stock*

| | Kuwait | Arabian |
|---|---|---|
| ° API | 54·4 | 54·9 |
| Engler distillation, ° F: | | |
| I.B.P. | 272 | 250 |
| E.P. | 378 | 393 |
| Wt % sulphur | 0·064 | 0·050 |
| F-1 clear octane no. | 32·4 | 29·7 |
| F-1 + 3 ml TEL | 55·2 | 54·6 |
| Vol %, Paraffins | 66·3 | 63·7 |
| Naphthenes | 19·8 | 20·0 |
| Aromatics | 13·9 | 16·0 |
| Olefins | — | 0·3 |

composition of the Platformates. Table VIII gives the tabulation of the principal data obtained, which include the octane ratings and the percentage of various classes of hydrocarbons.

TABLE VIII

*Platforming of Middle East Naphthas, Properties of Platformates*

| | KUWAIT | | | | |
|---|---|---|---|---|---|
| Debutanized Platformate, vol % yield | 87·5 | 85·3 | 84·1 | 81·0 | 76·6 |
| F-1 clear octane no. | 76·5 | 83·6 | 86·2 | 91·2 | 95·2 |
| F-1 + 3 ml TEL | 91·1 | 95·2 | 96·2 | 99·0 | (100·9)* |
| Aromatic content, wt % of charge | 38·1 | 44·1 | 43·6 | 46·6 | 47·0 |
| | ARABIAN | | | | |
| Debutanized Platformate, vol % yield | 83·9 | 82·3 | 79·8 | | |
| F-1 clear octane no. | 85·3 | 87·6 | 91·7 | | |
| F-1 + 3 ml TEL | 96·0 | 96·6 | 99·0 | | |
| Aromatic content, wt % of charge | 42·3 | 43·5 | 47·6 | | |

* Blending octane number; equivalent to +0·08 ml TEL.

There was little change in boiling range, and sulphur content was in all cases reduced to below 0·002 per cent. In general, conditions of increasing severity increased the octane ratings and the aromatic content, while decreasing the yield.

In Fig 6 the curves show a comparison of the products obtained to varying product yields when Platforming with those from thermally reforming a naphtha from a mixed base Mid-Continent crude oil. At 80 per cent gasoline yield the Platforming process gave a 95 octane number product, in contrast to a product of only 70 octane from thermal reforming of the same naphtha. The inclusion of polymer gasoline obtained from the gases produced in thermal reforming raised the octane number to 78, which was still well below that shown by the Platformed product.

Table IX shows typical results in Platforming

natural gasolines from two U.S. fields. Research octane numbers are raised from values around 36·6 and 43·5 clear to values of 86·7 and 96·2 respectively. The addition of 3 ml TEL/gal to the Platformate from the La Gloria field gave a product of slightly over 100 Research octane number.

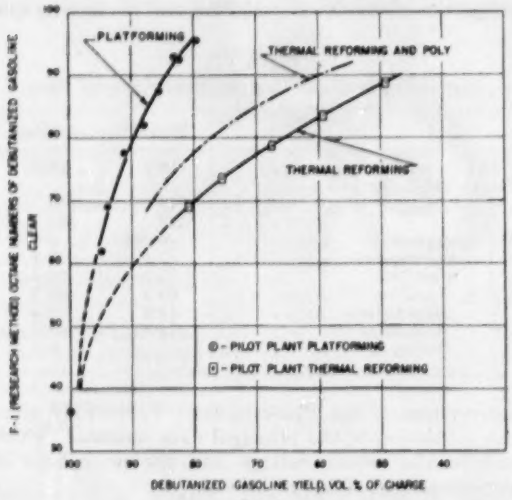

PLATFORMING
THERMAL REFORMING AND POLY
THERMAL REFORMING
⊙ - PILOT PLANT PLATFORMING
⊡ - PILOT PLANT THERMAL REFORMING
F-1 (RESEARCH METHOD) OCTANE NUMBERS OF DEBUTANIZED GASOLINE CLEAR
DEBUTANIZED GASOLINE YIELD, VOL % OF CHARGE

FIG 6

COMPARISON OF F-1 (RESEARCH) O.N. OF DEBUTANIZED GASOLINES FROM PLATFORMING AND THERMAL REFORMING OF MID-CONTINENT STRAIGHT-RUN NAPHTHA

The liquid product from Platforming is customarily depropanized to make a product designated as a " true Platformate." The lower boiling fractions of the original gasoline are then blended back with " true Platformate " to give a product representing full boiling range gasoline, which is referred to as " Platformate."

TABLE IX

*Typical Results from Platforming Natural Gasoline*

| | Feed source | | | |
|---|---|---|---|---|
| | Carthage (Texas) | | La Gloria (Texas) | |
| | Feed | Platformate | Feed | Platformate |
| Yield liq. vol % of charge | 100·0 | 91·5 | 100·0 | 85·9 |
| Engler distillation, ° F: | | | | |
| I.B.P. | 198 | 90 | 277 | 90 |
| E.P. | 388 | 420 | 342 | 402 |
| F-1 clear octane no. | 36·6 | 86·7 | 43·5 | 96·2 |
| F-1 + 3 ml TEL | 62·0 | 96·0 | 65·5 | (101·1) * |

* Blending octane number; equivalent to +0·1 ml TEL.

The products from Platforming gasolines and naphthas are unique among refinery products. They consist almost entirely of *iso*paraffinic and aromatic hydrocarbons. Both of these types of hydrocarbons have high octane ratings, and the paraffins have high susceptibility to improvement by additions of TEL. Because of the almost complete absence of olefins, Platformates have low gum-forming tendencies, and require only inhibitors to stabilize additions of TEL. The presence of large amounts of aromatics in the higher boiling portions of Platformed gasolines gives them octane ratings which are usually equal to or higher than those of the lower boiling, which is the opposite of corresponding straight-run and thermally cracked products. The exceptionally low sulphur content of Platformed gasolines is another outstanding characteristic.

Tests of Platformates in high compression ratio engines at high speed indicate that they are particularly adapted to function without knocking and will be specially suitable for use in automobile engines of the future. The octane ratings of Platformates are generally higher as engine speeds increase in contrast to either catalytically cracked or polymer gasolines, which show reduced ratings. In road tests made in a Chevrolet car, using a Platformed gasoline, the indicated octane number was 91 at 1000 r.p.m., while 96 octane number was obtained at 3000 r.p.m. When running on a catalytically-cracked gasoline the indicated octane number at 1000 r.p.m. was 94, while at 3000 r.p.m. it had dropped to 70. Similarly, a polymer gasoline dropped from 95 to 73 octane rating in the same speed range. In blends of Platformed gasoline with olefin-containing cracked gasolines the Platformed component acts to overcome the tendency of olefins to decrease in octane number as speed is increased.

Platformed gasoline is well suited for use in heavy duty truck service because of its high road antiknock values. The spark in truck engines can be advanced in maximum power position, whereas with lower antiknock gasolines, retarded spark is necessary to avoid heavy detonation. It has been noted in truck service that the engines are much cleaner after burning Platformed gasolines than when other gasolines have been used.

The Platforming process is admirably adapted to producing aviation gasoline components. The aromatics therein provide the surges of power needed in take-off and acceleration in airplane operation, while the *iso*paraffins produce power under cruising conditions. Several refiners are utilizing Platformates or aromatics extracted from them in aviation gasoline blends. The entire aromatic content can be used for blending, or its various components can be separated so that one or more can be used as chemical raw materials. Still other refiners use the entire aromatics production for chemicals and blend the non-aromatic fraction into aviation gasoline.

## AROMATICS PRODUCTION

Besides its suitability for markedly improving the octane rating of straight-run and natural gasolines or

TABLE X

*Composition of 140°–185° F Fractions from Various Straight-run Gasolines*

| | Ponca, Okla. | East Texas | Bradford, Pa. | Greendale, Mich. | Winkler, Texas | Midway, Calif. | Conroe, Texas |
|---|---|---|---|---|---|---|---|
| Hydrocarbons, vol %: | | | | | | | |
| Paraffins | 60 | 62 | 78 | 77 | 78 | 44 | 29 |
| Methyl*cyclo*pentane | 20 | 23 | 9 | 9 | 15 | 34 | 21 |
| *cyclo*Hexane | 16 | 12 | 12 | 11 | 6 | 21 | 31 |
| Benzene | 4 | 1 | 1 | 3 | 1 | 1 | 9 |
| Potential benzene from naphthenes | 22·3 | 20·7 | 13·8 | 13·0 | 12·0 | 32·2 | 34·5 |
| Percentage of 140°–185° F fraction present in $C_5$—360° F gasoline | 13 | 16 | 15 | 18 | 10 | 12 | 14 |

naphthas, the Platforming process is particularly well adapted to the manufacture of the aromatic hydrocarbons—benzene, toluene, the three xylenes, and ethylbenzene. The gasoline fractions employed for benzene manufacture boil within the approximate limits of 150° to 190° F (65° to 90° C). The aromatic and naphthenic contents of such gasolines vary widely with the crude oil source. Relatively higher temperatures and lower pressures are used because they tend to favour the dehydrogenation of naphthenes and reduce the extent of hydrocracking reactions. When hydrocracking is reduced, more heat must be supplied by the furnace. About 1000 B.T.U. are absorbed for each pound of naphthenes converted to aromatics by dehydrogenation. Some aromatics are produced by the dehydrocyclization of paraffin hydrocarbons. Any aromatics originally present in the charge stocks are relatively unaffected.

TABLE XI

*Platforming of 150°–190° F Cut from a California West Coast Stock to Produce Benzene*

| | Wt % | Potential wt % benzene yield |
|---|---|---|
| Charging stock: | | |
| Hexanes | 27·7 | |
| Methyl*cyclo*pentane | 36·6 | 44·4 |
| *cyclo*Hexane | 11·3 | |
| Benzene | 3·6 | 3·6 |
| $C_7$ naphthenes and paraffins | 20·8 | |
| | 100·0 | 48·0 |

INCREASING SEVERITY OF OPERATION

| | | | | | |
|---|---|---|---|---|---|
| Yield of liquid products | 95·2 | 94·9 | 94·0 | 94·1 | 93·3 |
| Benzene, wt % of charge | 36 | 38 | 39 | 41 | 44 |
| Toluene, wt % of charge | 12 | 12 | 13 | 13 | 15 |
| Benzene, % yield of theoretical | 75 | 79 | 81 | 85 | 92 |

Table X shows some analyses of fractions which boil within the range generally found most suitable for Platforming to produce benzene.

Table XI gives some data on the processing of a 150° to 190° F (65° to 90° C) fraction of a West Coast gasoline to produce benzene. The yield of benzene increased from 36 to 44 weight per cent of the charge as the yield dropped from 95·2 to 93·3 per cent with increasing severity of operation. It is interesting to note the large volume of hydrogen evolved in benzene production. The yield of hydrogen was about 3 per cent by weight of the charge, which corresponds to about 1740 cu. ft/brl.

When toluene is made by Platforming, gasoline fractions boiling approximately from 185° to 220° F (85° to 105° C) are employed, since these contain all of the $C_7$ naphthenes which may be present. Table XII gives data on the composition of gasoline fractions boiling from 185° to 220° F (85° to 105° C) from the same crude oils as were given in Table X, along with the calculated potential toluene yields from naphthenes and aromatics, which vary from 25·6 per cent in the Winkler, Texas, field charge to 64·1 per cent in the charge from Conroe, Texas.

In converting pure methyl*cyclo*hexane to toluene by

TABLE XII

*Stocks for Platforming to Toluene*

| | Ponca, Okla. | East Texas | Bradford, Pa. | Greendale, Mich. | Winkler, Texas | Midway, Calif. | Conroe, Texas |
|---|---|---|---|---|---|---|---|
| Hydrocarbons, vol %: | | | | | | | |
| Paraffins | 47 | 38 | 52 | 64 | 65 | 20 | 23 |
| 1,2-Dimethyl*cyclo*pentane | 2 | 2 | 2 | 2 | 4 | 3 | 2 |
| Trans, 1,3-Dimethyl*cyclo*pentane | 15 | 16 | 6 | 3 | 10 | 26 | 6 |
| Trans, 1,2-Dimethyl*cyclo*pentane | 5 | 6 | 6 | 1 | 8 | 10 | 1 |
| Methyl*cyclo*hexane | 21 | 27 | 24 | 18 | 10 | 30 | 36 |
| Ethyl*cyclo*pentane (est) | (3) | (4) | (4) | (3) | (1) | (5) | (5) |
| Toluene | 7 | 7 | 6 | 7 | 2 | 6 | 27 |
| Potential toluene from naphthenes | 34·2 | 40·8 | 31·2 | 20 | 24·5 | 55 | 37·1 |
| Percentage of 185°–220° F fraction present in $C_5$—360° F gasoline | 23 | 25 | 24 | 23 | 15 | 20 | 27 |

dehydrogenation, the theoretical yield is 83·3 per cent by volume. The octane rating of methyl*cyclo*hexane is 67·2, while that of toluene corresponds to a blending octane number of 110·5 (equivalent to +5·8 ml TEL). The research octane number of ethyl*cyclo*pentane is 31·2 and the octane ratings of dimethyl-*cyclo*pentanes vary between 79·2 and 92·3.

TABLE XIII

*Platforming a 202°–224° F Cut from a Gulf Coast Stock for Toluene*

| | | |
|---|---|---|
| Charge, composition, wt % : | | |
| $C_7$ and $C_8$ paraffins | 28 | |
| $C_7$ and $C_8$ naphthenes | 62 | |
| Toluene | 10 | |
| Products, wt % of charge : | Run No. 1 | Run No. 2 |
| Gas | 14·0 | 14·4 |
| $C_4$ and $C_5$ paraffins | 4·3 | 5·1 |
| $C_6$, $C_7$, and $C_8$ paraffins and naphthenes | 17·2 | 18·5 |
| Benzene | 0·9 | 0·9 |
| Toluene | 55·8 | 53·3 |
| $C_8$ aromatics | 7·8 | 7·8 |

Table XIII contains significant data obtained from a commercial plant operating on a Gulf Coast stock to produce toluene. Two runs were made on a narrow boiling range stock boiling from 202° to 224° F (95° to 105° C). The weight per cent yield of toluene was 55·8 per cent in the first run and 53·3 per cent in the second. Approximately 1200 cu. ft/brl of charge or 2·4 per cent by weight of hydrogen were produced.

When the Platforming process is used for making xylenes and higher boiling aromatics, gasoline fractions boiling from approximately 220° to 280° F (105° to 140° C) are included in charging stock. Table XIV contains data obtained in a pilot plant run on a 220° to 285° F cut. Yields of $C_8$ and higher aromatics are given as volume per cent. About 800 cu. ft. of hydrogen were produced from each barrel of charging stock.

TABLE XIV

*Platforming a 220°–285° F Cut from a Gulf Coast Stock for Xylene*

| | Volume % $C_8$ and higher aromatics | |
|---|---|---|
| Charge : | | |
| $C_8$ aromatics | 8·0 | |
| Higher aromatics | 2·2 | |
| | | 10·2 |
| Product : | | |
| Vol of $C_8$ and higher : | | |
| *o*-Xylene | 4·1 | |
| *m*-Xylene | 10·3 | |
| *p*-Xylene | 5·3 | |
| Ethylbenzene | 5·8 | |
| Higher aromatics | 7·4 | |
| | | 32·9 |

The Udex process, in which aromatics are recovered by solvent extraction with aqueous solutions of diethylene glycol, is particularly well suited for use in connexion with the Platforming process. Diethylene glycol has a melting point of 13·1° F (−10·5° C) and a boiling point of 472·6° F (244·8° C). It mixes with water in all proportions. The water solutions are excellent solvents for the aromatics, but dissolve practically no paraffins. Unsaturated compounds are not present in Platformates in sufficient quantities to introduce difficulties. However, aromatics can be recovered from cracked oils containing olefins by extracting after hydrogenating the olefins. This method is being applied to olefin-containing aromatic concentrates which are by-products of ethylene production by high temperature cracking.

The flow in a Udex extraction unit is shown in Fig 7. The process uses an efficient multi-stage countercurrent extraction column of novel design developed especially for this purpose. Because temperature and pressure are low and the system is non-corrosive carbon-steel equipment is used throughout the unit. Solvent is fed at the top of the column; hydrocarbon feed at an intermediate point; and hydrocarbon reflux at the bottom. The rich solvent is taken to a stripper, wherein the dissolved aromatics are separated from the solvent, the latter being recirculated to the extraction column. Vapours from the stripper are condensed and separated into two phases. The water phase is used in part to wash traces of dissolved glycols from the raffinate; the remainder is returned to the stripper. The hydrocarbon phase from the stripper receiver is a mixture of aromatics from which the benzene, toluene, and a mixed ethylbenzene–xylene fraction are separated. Benzene, toluene, and *o*-xylene are readily separated by distillation. The *meta* and *para* components of the xylene fraction can be separated by fractional crystallization.

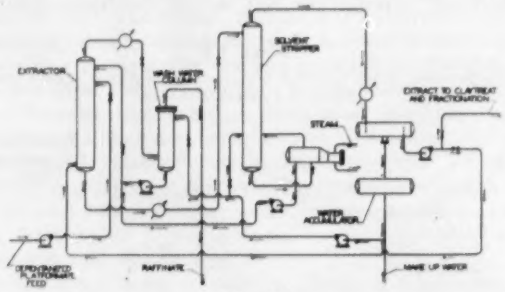



FIG 7

FLOW DIAGRAM OF UDEX EXTRACTION UNIT

Clay treater and three fractionators in series for separating aromatics not shown.

The high boiling point of the glycol is an advantage, since the aromatics can be readily recovered from it by distillation without vaporizing the glycol, the boiling point of *o*-xylene being 292° F (145° C). Thus, a minimum of heat is required for solvent regeneration. The effectiveness of the diethylene glycol solvent is demonstrated by the recovery of 99 per cent of the

benzene in a Platformate containing only 25 per cent benzene by volume.

Aromatics made by the Platforming process and recovered by the Udex method are of exceptional purity. Benzene, toluene, and xylenes, which meet the rigid specifications of the American Society for Testing Materials and the American Chemical Society for reagent chemicals, are being commercially produced in tank car lots. Benzene and toluene not only meet the requirements for nitration grade products but they are also used in manufacturing chemicals which require raw materials of even higher purity. The boiling ranges of benzene and toluene made by the Platforming–Udex combination process are less than 1° C. The benzene contains less than 0·1 per cent non-aromatic hydrocarbons, and the toluene contains less than 0·05 per cent non-aromatics. Toluene from Platforming and recovered by the Udex process can be used for the manufacture of cortisone, the anti-arthritic hormone. It is being used in the manufacture of saccharin. Petroleum-based toluene is also used for the manufacture of pure benzoic acid and other derivatives. A U.S. Government arsenal has reported that toluene recovered by Udex extraction is the purest they have processed.

The raffinate remaining after extraction of aromatics has a high octane rating because of the presence of *iso*paraffin hydrocarbons and is blended into gasolines.

## FUTURE OF PROCESS

The versatility of Platforming provides refiners with a buffer against changing economic conditions. If for a period of time the market for aromatics is depressed, a Platforming unit can be converted to gasoline production and conversely. Units can be designed for profitable operation in any size of refinery. Those now being built range from 500 to 29,000 b.d. charging capacity. At present some units are constructed for production of gasolines, some for aromatics, and others for blocked-out operations in which gasolines and aromatics are produced alternately. Although temporary recessions in demands for either high octane gasoline or aromatics are possible, every long-range forecast predicts large increases in requirements for both in the future. The UOP Platforming process is an excellent addition to any refinery for both the present and future.

# DISCUSSION

**E. Le. Q. Herbert:** "Good wine needs no bush" is a good and wise old saying, and in the Platforming process, if I may use the analogy, we have indeed an outstanding vintage. Brewer paraphrases the saying thus: "a good article will make itself known without being puffed;" we will all agree, I think, that the Platforming process certainly needed no "puffing," as is instanced by the quite remarkable way in which it was and is being taken up and applied by the petroleum industry—remarkable even for an industry which has a reputation for doing things in a big way and quickly. Some fifty units, large and small, are already in operation, not only throughout the U.S.A. but in many different parts of the world, and another fifty or so are presently under construction or being developed.

I do not think that it is any exaggeration to say that Platforming has probably been the outstanding process development in the industry since the advent of catalytic cracking in the early years of the war.

Shakespeare, in "As You Like It," says: "If it is true that good wine needs no bush, 'tis true that a good play needs no epilogue"—nor does a good process; nevertheless, there is no question in my mind that such an all-important development in our industry—such an outstanding process that is already playing so great a part in almost every refiner's operations and is undoubtedly destined to play an even greater one—merits full and detailed discussion by experts of the many interesting points which arise from its increasing application and development.

We are, then, more than grateful to Dr Egloff for coming over here to give us his paper, and I think too that the Institute is to be congratulated on having invited him to do so, thus giving us all this opportunity of discussion and of putting our questions to him.

Now I am, of course, aware that it is our custom when papers of this standard and importance are being delivered to invite someone to open the discussion—but I was, frankly, somewhat embarrassed and not a little puzzled as to why the Papers Committee should have honoured me in this way: for an honour and indeed a privilege I believe it is to be asked to do so in the case of so distinguished an author as Dr Egloff.

There are others who are better qualified, technically and otherwise, to do so, and my embarrassment remains when I see so many of them here with us tonight.

However, I felt I could but accept as without doubt the Group I serve has been in the forefront of the companies in applying the Platforming process. I think I am right in saying that the unit at the Wood River Refinery (Shell Oil) was almost the first, if not the first, to operate in the U.S.A.; and the Houston Refinery unit was one of the first major units to be constructed and operated primarily for the production of aromatics.

Then in the U.K. the Platformer at Stanlow which came on stream early in December 1953 was the first to do so either in the U.K. or Europe, and currently another unit is under construction at Shell Haven, while, in the Group as a whole, several others are either in construction or being planned in various countries.

Now, turning more specifically to Dr Egloff's paper, I was particularly interested in his opening sentence, in which he points out that the Platforming process is solving or helping to solve three of the most important problems facing refiners today—(1) increasing octane requirements, (2) production of aromatics, and (3) production of hydrogen either for upgrading other stocks or for other purposes, *e.g.* $NH_3$, because the Stanlow unit may possibly be unique in that it is performing all three of these functions.

It was built primarily and is operating for the production of high octane aviation gasoline components—but there is currently being built alongside it a hydrodesulphurizer unit—using the new "trickle phase" process which will use the $H_2$ from the Platformer. Thirdly, a xylene fraction is being separated from the Platformate production for supply to I.C.I. at Wilton, who will utilize the *p*-xylene for conversion to dimethyl terephthalate in the production of Terylene.

Dr Egloff is, of course, fully aware of the position

regarding the construction and/or the planning of additional Platformers by the various major oil companies in the U.K., in Europe, and other parts of the world. He is also well aware that to refiners outside the U.S.A. and Venezuela, Middle East crude and feedstocks are in general the basis—indeed the foundation—of all their operations. Most of us here then have, I am sure, been especially interested in the information given in the paper regarding the Platforming of Middle East feedstocks.

I think it is fair comment, however, to say that in spite of the repeated mention of the Platforming of Middle East naphthas and the data given, the advantages and main features of the process are reviewed mainly on the basis of U.S. commercial experience using feedstocks of U.S. origin. This is perfectly understandable—but it is necessary to recognize that the Middle East feedstocks available to European and other refiners have quite different properties from those generally available in the U.S.A. Notably, there is the difference in average naphthene content—while the latter is of the order of 35 per cent wt, the Middle East naphthas contain only around 20 per cent (perhaps 25 per cent at most). I think the repercussions of this difference can be summarized briefly as follows:

Firstly, the average catalyst life in the U.S. plants is stated to be about 71 brl/lb (in passing I might mention that this figure is well supported by the Stanlow unit, which has been continuously on stream since it started and whose catalyst life presently exceeds this figure with no indication yet of approaching exhaustion; however, the unit is processing a specially selected high naphthene content feedstock of Venezuelan origin).

The average F.1 octane number at present being produced in commercial Platformers is said to be of the order of 85 (or less).

Now in order to produce Platformate of similar quality from Middle East naphthas, with their lower naphthene content, a considerably higher severity will have to be applied and will result in a shorter catalyst life.

In this connexion, the yield–octane relationships given for Kuwait naphtha in Tables V and VII are very interesting, but I suggest the tables lack one very important feature, namely catalyst life data. Will, in fact, the very high octane numbers shown be commercially realizable with a practical catalyst consumption?

**Dr G. Egloff**: I am grateful for the penetrating comments and the questions raised by Mr Herbert which help to bring a broader perspective to the subject of Platforming.

First, I would like to correct a possible misunderstanding regarding the average octane number produced in the U.S. plants. The actual octane number for commercial units has averaged 95–98 leaded. The 85 O.N. mentioned in the question refers to the clear octane number, which actually ranges between 85 and 90.

In answer to the question, the high octane numbers shown are being realized with practical catalyst lives. A prolonged run in a large-size pilot plant, processing Kuwait naphtha and making Platformates having clear octane numbers ranging from 88·5 to 90·5 and 97·5 to 98·5 leaded, was carried to about 25 brl of naphtha per pound of Platforming catalyst without appreciable change in activity of the catalyst.

We are accumulating a substantial amount of information on the commercial processing of Middle East stocks. In five commercial units currently processing Middle East stocks, three are operating to make regular grade gasolines and have obtained long lives. Two of these three units are still operating after having reached catalyst lives of 102 and 120 brl/lb, while another unit has changed catalyst after completing a run exceeding 250 brl/lb. A fourth unit operating to make premium gasoline has just started recently, and no life data are therefore available except to say that the unit is performing very well at this high severity operation. The fifth unit is operating on a feed consisting of 75 per cent of Middle East stocks and is producing a premium gasoline. The life of the catalyst at present is in excess of 65 brl/lb, and the unit is still on stream.

In addition, our experience in the U.S.A. also includes the Platforming of stocks similar to and in one case actually lower in naphthene content than the Middle East stocks. In these operations, catalyst lives of 60 to 80 brl/lb have been obtained consistently while producing premium gasolines.

**E. Le Q. Herbert**: The average $H_2$ production for U.S. naphthas is stated to be of the order of 500–600 SCF/brl. For Middle East naphthas this figure will be approximately halved—thus the process's potential for catalytic hydrogenation of other refinery stock or for $NH_3$ production or other chemical use is necessarily reduced.

**Dr G. Egloff**: The average hydrogen production from Middle East stocks obtained in commercial operation is of the order of 300 to 400 cu. ft/brl.

**E. Le. Q. Herbert**: The average purity of the $H_2$ produced from Middle East naphthas is, I believe, less than that obtained from high naphthene content stocks, such as are available in the U.S.A., and may thus lead to certain complications in using the $H_2$ for these other purposes.

**Dr G. Egloff**: The purity of the hydrogen stream being obtained commercially from Middle East stocks ranges between 80 and 90 per cent, and is essentially the same as that obtained from other stocks.

**E. Le. Q. Herbert**: The figures quoted by Dr Egloff in regard to the trend towards high compression ratios in automotive engines in the U.S.A. are interesting, and I hope that some of the engine experts here tonight may have something to say—or some questions to raise on this matter. The premium gasoline octane number trend in the U.S.A. mentioned seems to agree with what we have heard in the current rhyme in refiner circles there, *i.e.* 95 in '55 to 98 by '58, and certainly adds point to the urgent need for high octane blending agents.

Here in the U.K. the current pattern is not much different, and the trend may well be along the same lines. Average compression ratios of automobiles in the U.K. is about 7·5. However, the export market for automobiles tends to restrict manufacturers from further increases; it is difficult to manufacture a high compression engine for U.K. consumption which can easily be fitted with a lower compression head to make it suitable for export to countries where lower octane fuels are currently marketed. However, no doubt there will be a trend upwards, but it is difficult to express this in quantitative terms.

The high performance of Platformate at high engine speeds in comparison with catalytically cracked and polymer gasolines mentioned in the paper (p. 74) is very interesting. I wonder if Dr Egloff has any data to show the extent to which this behaviour is maintained in blends with catalytically cracked and polymer gasolines? Would such a blend retain the "road octane" advantage of pure Platformate in direct proportion to the Platformate content of the blend?

**Dr G. Egloff**: Yes. The road data were obtained in a 1949 Oldsmobile using a General Motors research engine with 10 : 1 compression ratio. Figs 8 and 9 are made up for engine r.p.m. versus road octane numbers.

With regard to the Platformate-catalytically cracked

and poly gasoline blends (all with 3·0 ml TEL/gal) the 100 per cent Platformate curve at 800 r.p.m. is 88 octane number and increases to about 98 O.N. at 2500 r.p.m. The 100 per cent catalytically cracked curve at 800 r.p.m. is about 98 O.N. and decreases to about 92 O.N. at 2500 r.p.m. Blends of these stocks in ratios of

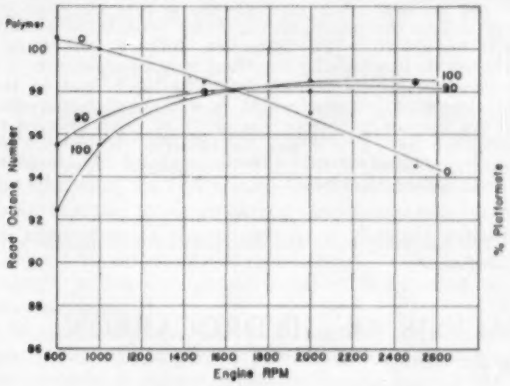



FIG 8

PLATFORMATE–POLYMER BLENDS. 1949 OLDSMOBILE (RESEARCH ENGINE, 10:1 COMPRESSION RATIO). ALL WITH 3·0 ML TEL/U.S.GAL.

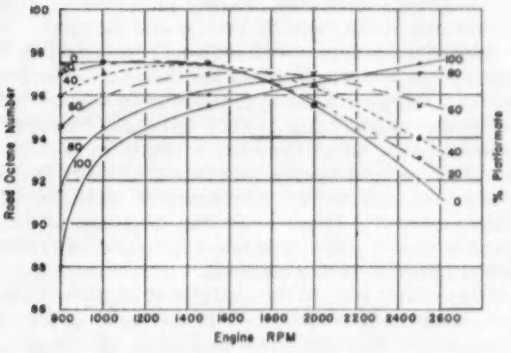



FIG 9

PLATFORMATE–CATALYTIC CRACKED GASOLINE BLENDS. 1949 OLDSMOBILE (RESEARCH ENGINE, 10:1 COMPRESSION RATIO). ALL WITH 3·0 ML TEL/U.S.GAL.

20/80, 40/60, 60/40, and 80/20 fall between the curves for 100 per cent components in direct proportion to the Platformate content of the blend. Two curves are included, one on catalytic cracked gasoline blends, the other on polymer blends.

A similar effect is noted for the Platformate–polymer blend data. The Platformate used in this case rated about 92 O.N. number at 800 r.p.m. and increased to about 99 O.N. at 2500 r.p.m. The polymer rated slightly over 100 at 800 r.p.m. and decreased to about 94 O.N. at 2500 r.p.m. The one blend (10 per cent polymer, 90 per cent Platformate) falls between the two component curves in proportion to the Platformate content of the blend.

**E. Le. Q. Herbert :** Finally, certain other catalytic reforming processes employ low pressure and catalyst regeneration and claim thereby to reach a higher octane ceiling. Does Dr Egloff think that in view of the continuing trend to higher octane requirements, it will become more economic to employ Platforming as a low pressure, regenerative process, especially in the case of feedstocks of low naphthene content such as Kuwait naphtha?

What are the chances of a Platforming catalyst capable of regeneration being available in the near future?

**Dr G. Egloff :** To the operating refiner, one of the more important advantages of Platforming is its ability to produce high octane number products without the use of the expensive, complex, and troublesome operation of regeneration. Present octane requirements are being met easily and economically by the process without resorting to periodic regeneration. As octane requirements increase, modifications in operating technique are available, and will be used to produce such higher octane numbers in continuous uninterrupted operations without readopting the older regenerative methods.

**A. Jeffrey :** Could I just ask what base is the platinum? The catalyst, we take it, is not pure platinum, so what base is it on?

**Dr G. Egloff :** The catalyst comprises a specially prepared composite of aluminium oxide, halogen, and platinum.

**W. Newby :** Can the Udex process be used for the extraction of $C_8^+$ aromatics?

**Dr G. Egloff :** Yes. The Udex process is being used commercially for the extraction of $C_8^+$ aromatics.

**W. Newby :** Will Unifining of the charge increase catalyst life at either (*a*) low severity or (*b*) high severity?

**Dr G. Egloff :** Yes. In cases where excessive quantities of undesirable elements are present in the feedstock, Unifining of such feedstocks will increase the life of the Platforming catalyst, both at low and high severity operation.

**W. Newby :** What is the effect of pressure on temperature of operation and catalyst life with Middle East feedstocks for the production of 90 Research O.N. Platformate?

**Dr G. Egloff :** As the pressure is increased, slightly higher temperatures are required to obtain a given octane number. Increasing the operating pressure generally will extend the catalyst life.

**E. Hargraves :** Has Dr Egloff ever encountered the phenomenon of hydrogen blistering of the metal surface in the Platformer? During the pickling of steel in an acid solution the hydrogen formed may enter the metal in the atomic state. When occluded in the metallic lattice diffusion outwards is prevented by the formation of molecular hydrogen, and in consequence the surface of the metal develops blisters. If this reaction may take place in the Platformer, is it possible to prevent this by the use of low chromium alloy steel?

**Dr G. Egloff :** The type of hydrogen blistering referred to in the question and encountered in catalytic cracking, pickling of steel, etc., has not been encountered in the Platformer. The tendency for hydrogen to attack carbon steel was recognized before the first Platforming unit was designed, and provisions were made in the Platforming equipment design to avoid any difficulty from this source. Among these provisions is the use of low chromium alloy steel.

The meeting then closed with a unanimous vote of thanks to Dr Egloff.

# THE INSTITUTE OF PETROLEUM

An Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London W.1, on 10 November 1954, the Chair being taken by R. B. Southall, a Vice-President of the Institute.

**The General Secretary** read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting, and gave notice of the date of the next meeting.

**The Chairman,** introducing the author of the paper to be presented said: In the absence of the President, I have unexpectedly been asked to take the Chair at this meeting, and I want to convey to you first his apologies for not being here.

We have three friends with us tonight from an associated industry, and I am sure that we are all looking forward to what they have to tell us with great interest. Our friends have brought with them an unusual array of apparatus, which will undoubtedly add to the interest of the meeting. The arrangement is that Dr Bradford will deliver the paper, during which some lantern slides will be shown. The discussion follows immediately afterwards in which Dr Bradford may be assisted by his colleagues, Messrs Harvey and Chalkley; and at the conclusion of the questions, there will be a demonstration of the various instruments which they have brought to enlighten us. I now ask Dr Bradford to present his paper, entitled "The Chromatographic Analysis of Hydrocarbon Mixtures."

The following paper was then presented in summary by the author:

## THE CHROMATOGRAPHIC ANALYSIS OF HYDROCARBON MIXTURES *

By B. W. BRADFORD, D. HARVEY, and D. E. CHALKLEY †

The term "chromatography" has established itself as a convenient generic description for analytical separations, depending upon differential sorption or solution of the components of a flowing mixture with respect to a stationary solid medium, and several variations of the method have become established for different purposes. This paper deals briefly with the main chromatographic methods which have been found useful in the analysis of hydrocarbon mixtures, and in more detail with some recent developments which are providing powerful new techniques in this field of analysis. Several comprehensive text-books and reviews of the already very extensive literature on chromatography have appeared in the past few years,[1, 2, 3] and it is unnecessary to devote much attention here to the history of the subject or to the general principles on which it is based.

The work which has been done with hydrocarbons falls into three main types:

(1) liquid-phase separation on columns of solid absorbents;

(2) vapour-phase separation on columns of solid absorbents;

(3) vapour-phase separation on composite partition columns.

Liquid-phase techniques were developed first, but few have become established as routine or regularly used analytical methods. Vapour-phase techniques have developed rapidly in recent years, and the greater part of this contribution is devoted to them.

### LIQUID-PHASE METHODS

In addition to the general literature on chromatography cited above, liquid-phase chromatographic separation of hydrocarbons has been reviewed by Juhola,[4] van Nes and van Westen,[5] and important investigations have been recently published by Fink, Lewis, and Weiss,[6] and by Tenney and Sturgis.[7]

Liquid-phase separations are usually operated at, or near, room temperature, and are therefore most conveniently applicable to hydrocarbons in the medium molecular weight range. They have also frequently been applied, using the elution method, to higher molecular weight species in solution. Direct liquid-phase separations by displacement methods are chiefly of utility in pre-separation of groups of compounds from a mixture before application of further fractionation by other methods. A number of applications of this type to the analyses of highly complex petroleum cuts is described in a recent paper by Rampton.[8] The complete separation of individual hydrocarbons by liquid-phase chromatography can usually be accomplished only by special procedures, such as the use of successive eluants; examples are the separation of polynuclear aromatic hydrocarbons [9] and of a $C_{13}$–$C_{16}$ mixture.[10]

Useful though liquid-phase separations are in the study of specific problems, few have become established as routine analytical methods. One exception is the well-known Mair method [11] for the determination of aromatics in gasoline; this is slow, requiring between 4 and 8 hours for a single determination, and when separate group fractions are not required it is preferable to use a more convenient and rapid micro-method with visual indicators which has recently been developed.[12] It is a general disadvantage of liquid-phase operation that separations must be carried out very slowly, and the course of separation is usually followed by refractive index measurements on succes-

* MS received 13 September 1954.

† Imperial Chemical Industries Ltd., Billingham Division.

sive small fractions. Continuous methods of indication have been devised,[7] but involve the immobilization of elaborate physical apparatus for the long periods required for separations. Moreover, there are inherent limitations to the accuracy of liquid-phase separation, due mainly to the difficulty of obtaining sharp separation between components.

## VAPOUR-PHASE METHODS

The separation of gases or vapours by differential adsorption on, for example, charcoal, is a classical method, and has been used in various forms, both in the laboratory and on a large scale. A pioneer automatic analyser for hydrocarbon gas streams was based on adsorption of the sample on a charcoal column followed by displacement development with mercury vapour, a hot-wire gauge being used to trace the chromatogram.[13]

More recently the two techniques of adsorption and partition chromatography have both been applied to the problem of analysing volatile liquids, but the gas–liquid partition method introduced by James and Martin [14] has some important advantages.

In adsorption chromatography the stationary phase consists of a column of adsorbent, *e.g.* active charcoal, while the mobile phase is a permanent gas, such as nitrogen. Volatile substances may be eluted from such columns, maintained at an appropriate temperature, but the non-linear isotherms of most substances on charcoal give rise to asymmetric elution peaks, and sharp separations are difficult to obtain. Attempts have been made to overcome this difficulty by the use of thermal desorption, but a more successful approach has been to apply the method of displacement development, introduced by Claesson [15] and since developed in the U.K. by Phillips [16, 17, 18] and his co-workers. These authors have described the separation of a wide variety of organic compounds. The mixture to be analysed is vaporized in a stream of nitrogen and fed to the column where it is adsorbed. The nitrogen stream is next saturated with a high-boiling liquid which is more strongly adsorbed than any of the components of the mixture. These components are then displaced from the column, emerging successively, in the majority of cases, in the order of their boiling points, the most volatile components being displaced first. If the exit nitrogen stream is passed through a thermal conductivity cell connected to a high-speed pen recorder the components appear on the recorder chart as a series of steps, the height of each of which is characteristic of the component and the length proportional to the amount present. By means of columns consisting of sections of decreasing diameter very sharp fronts are obtained, and substances can be separated whose boiling points differ by as little as 0·3° C.

This displacement technique, however, suffers from two disadvantages. First, the column must usually be replaced after each run and, secondly, substances with similar or nearly similar thermal conductivities, *e.g.* isomers, will give similar step heights, and if displaced one after the other are indistinguishable. In their paper introducing the technique of liquid–liquid partition chromatography, Martin and Synge [19] suggested that the moving phase might be replaced by a permanent gas, and pointed out that the low viscosity of such a gas would enable long columns to be used. The first work along these lines was reported by James and Martin [14] in 1952. In this technique the charcoal adsorbent was replaced by a non-volatile liquid held on a solid support, such as kieselguhr, while the mobile phase was a gas as before. Volatile components of a mixture are eluted from such a column at rates proportional to their respective vapour pressures over the column liquid. The process of separation is thus clearly analogous to extractive distillation, and in fact the efficiency of the column may be expressed in terms of the number of theoretical plates; on this basis efficiencies as high as 1000 plates in a 4-ft column are possible.[14] By choosing an appropriate liquid for the stationary phase it is possible so to influence the differential vapour pressure between components as to separate closely boiling or azeotrope-forming compounds. Other advantages are the speed with which separations may be achieved, and the extremely small quantities of a mixture required for analysis, the lower limit being set only by the sensitivity of the detecting device and not by the column. Two difficulties associated with displacement columns, namely, the necessity for frequent change of column and the inability to distinguish between similar step heights, do not occur in the partition technique. After the complete elution of one sample a partition column may be immediately used again for the next. Thus, provided that the stationary phase is stable and non-volatile under the operating conditions, one column may be used for an indefinite number of analyses. If separation is complete each eluted substance leaves the column as a discrete band, and using a thermal conductivity cell as a detecting device, each substance gives a concentration curve or elution " peak " on the recorder, provided only that its thermal conductivity differs from that of the carrier gas stream. Two substances with similar conductivities will if resolved give separate peaks which are easily distinguishable.

Following upon the work of James and Martin, Ray [20] examined the behaviour of a number of aromatic and non-aromatic hydrocarbons, ethers, and alcohols, and achieved many separations previously found impossible by the liquid-phase technique. He introduced a number of improvements into the apparatus, including the use of a rubber septum for adding samples to the column, and adopted the use of an internal standard as an aid to quantitative measurement.

With these modifications the vapour-phase partition method was much improved in speed and convenience, and soon found to have exceptional power in separating the components of a wide variety of mixtures of gases and of liquids of medium molecular weights. It was also found to be capable, when closely controlled,

of giving quantitative results of good accuracy and to be adaptable to routine conditions. The apparatus and methods of operation have been standardized, and are described in a following section. Reference is first made to some features of chromatographic separation which are important in the vapour-phase partition technique.

## THE SEPARATION PROCESS

The mode of action of vapour-phase chromatographic separation is apparently simple, but the physical chemistry of the process cannot yet be said to be completely understood, and the technique has developed empirically. A better understanding is necessary before full advantage can be taken of its potentialities, especially in the direction of increased resolving power. A brief account is therefore given of some work which is in progress on this aspect.

A basic advantage of the partition method over adsorption lies in the different types of distribution isotherm involved. In adsorption chromatography, even in vapour-phase operation, the isotherms are usually far from linear. In partition chromatography, distribution depends upon solution effects and not interface effects; the isotherms should therefore be linear with concentration. The experimental evidence so far accumulated confirms this expectation.

With this simplifying assumption it was first pointed out by James and Martin that the time taken for any particular component to emerge from a given column can be related to its partition coefficient between the mobile and stationary phases. It can be shown by simple analysis that the relative separation rate of a component can be expressed as:

$$R_F = \frac{\text{Time for solvent front to emerge}}{\text{Mean residence time of component}} = \frac{m}{m + \alpha}$$

where $m$ is the volume ratio of the mobile and stationary phases, and $\alpha$ is the partition coefficient of the component between mobile and stationary phases.

To test this a series of measurements was made with propane on a column of kieselguhr impregnated with tri-*iso*butylene using nitrogen as eluant gas. Operating conditions ranged from 20 to 70 mm pressure and $-20°$ to $+20°$ C. Values of $\alpha$ were calculated from these measurements, and from the determined value of $m$. At 20° C, for example, the values of $\alpha$ found ranged from 13·8 at the lower pressure to 13·6 at the higher. The measured value of the solubility of propane in bulk tri-*iso*butylene at 20° C was found to be 13·8 in the same units; it is clear therefore that simple solution is involved. As a further check on this, heats of solution in the column were derived from the temperature coefficient of $\alpha$, and found to be practically identical with the heat of vaporization of bulk propane. Similar results were obtained with propylene. The calculated thickness of the film of tri-*iso*butylene absorbed on the kieselguhr is $10^{-3}$ mm only, but in spite of this, solution occurs normally with no appreciable interaction between solutes and the solid support, and the relative rates of separation of two components are governed only by their relative solubilities in the liquid component of the stationary phase.

When considering the separation of two components of closely similar solubility, however, other factors must be taken into account. The problem is analogous to the resolution of adjacent spectral bands, and is affected to a considerable extent by the width and shape of the chromatographic peaks. Assuming only that the rate of partition is at all times proportional to the distance from partition equilibrium and that broadening of the chromatogram is the result of diffusional spread in the two phases and through the boundary layer, it can be shown that the peak should be a symmetrical Gaussian function (*cf* Martin and Synge[19]). In practice this is not found to be true, the peaks are not perfectly symmetrical and the front slope is steeper than the rear slope. It is not easy to demonstrate this unequivocally, since instrumental errors can readily obscure the true shapes of the peaks, but it has been established by separate measurement of the front and rear slopes of a very broad peak. Some additional rate factor is therefore operating, and work is still in progress to discover what it is.

For a given column packing, resolution increases with increase of residence time, but this is accompanied by diffusion broadening of all peaks. A limit of resolving power is therefore reached when conditions are such that increase of residence time broadens two adjacent peaks at the same rate as their centres are separated. When this occurs, further increase of resolution can be achieved only by using a more sensitive column or by taking off the unresolved fractions and analysing them by other means. Some examples of this are given later.

## DESCRIPTION OF APPARATUS AND METHOD

The techniques for dealing with liquid and gas samples are slightly different, and are dealt with separately for convenience.

## ANALYSIS OF LIQUID SAMPLES

The apparatus used for liquid analysis is shown diagrammatically in Fig 1. A stream of nitrogen from a cylinder flows in turn through a capillary tube flowmeter, a needle type control valve, one of a pair of thermal conductivity cells, the chromatographic column, the second thermal conductivity cell, an exit control valve, a vacuum pump, and thence to atmosphere. Mercury pressure manometers are fitted to both inlet and exit sides of the column. The double-sided thermal conductivity cell (heated to prevent condensation of high-boiling components) feeds its out of balance potential to a Brown electronic recorder.

The chromatographic column consists of a glass U-

tube 6 ft long and $\frac{1}{4}$ inch internal diameter, fitted with a short side arm for the inlet flow of carrier gas, and a rather wider $\frac{3}{8}$ inch bore length of tubing, to which is attached the rubber serum-bottle cap. The column is packed with a mixture of kieselguhr (Celite 545, Johns, Manville & Co. Ltd.) graded as described by James and Martin,[14] and the selected liquid phase in known proportions, usually 30 per cent by wt liquid. The mixture is packed down to a known density (0·43 g/cc $\pm$ 0·03), and the two ends of the column plugged with glass wool. The column is surrounded with an air jacket contained by two concentric glass tubes on the inner of which is wound several turns of resistance wire connected to a regulated supply of 50 volts, A.C. This arrangement has been found to give steady and reproducible conditions, and is more convenient than the vapour jackets used by other workers.

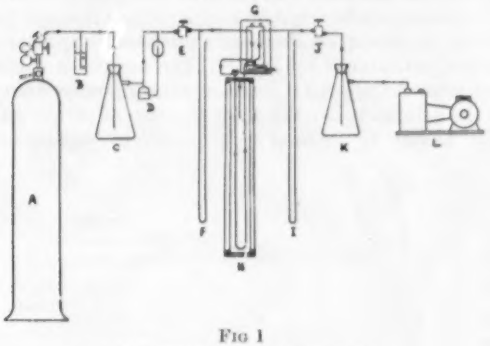



FIG 1

LINE DIAGRAM OF APPARATUS

A Nitrogen cylinder
B Bubbler
C Buffer vessel
D Flowmeter
E Needle valve
F Manometer
G Thermal conductivity cell
H Column
I Manometer
J Needle valve
K Buffer vessel
L Vacuum pump

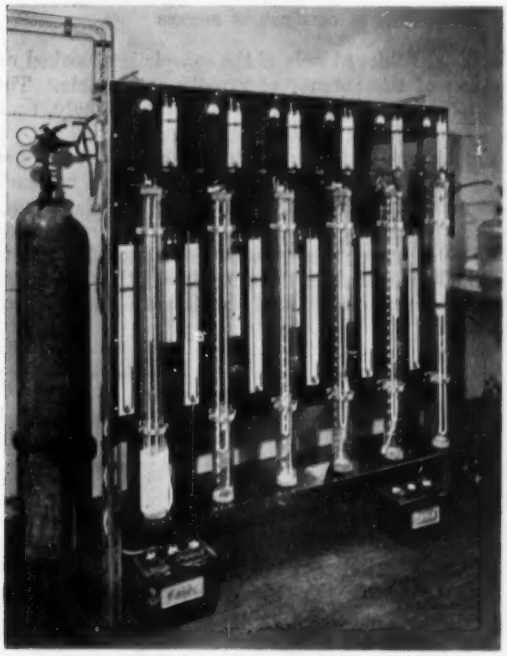


FIG 2

SIX-COLUMN APPARATUS

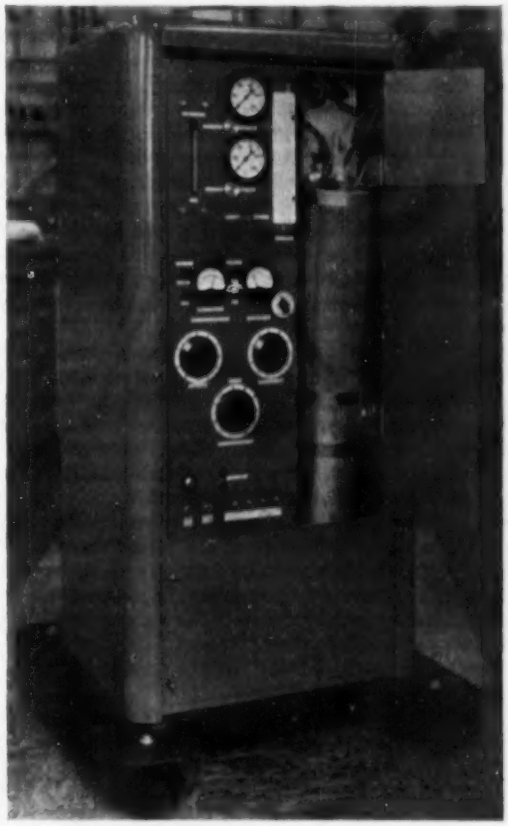


FIG 3

PROCESS LABORATORY APPARATUS

For routine analytical laboratory work it is convenient to use a group of six such apparatuses mounted upon a single panel (Fig 2). For process laboratory work a more robust single-tube apparatus has been evolved (Fig 3).

The retention volume of a particular component, *i.e.* the volume of carrier gas that must be passed before the elution " peak " or point of maximum concentration of the component is reached is a constant for a given column under given conditions. It is thus possible to identify a component by putting the pure substance on to the column under similar conditions.

If the substance is not available it may still be possible to carry out an identification if the homologous series to which the substance belongs is known. James and Martin have shown that for a homologous series on a given column a plot of the logarithm of the retention volume against the number of carbon atoms of each member is an approximate straight line, and the carbon number of a component may be determined in this way. Similarly, James and Martin have shown how the class of an amine (primary, secondary, or tertiary) may be determined by a comparison of its retention volume on two or more different liquids. Alternatively, it is possible to collect pure components in a suitable fraction collector, and identify them by some other method.

The procedure for establishing conditions for a quantitative separation of a known mixture is illustrated by the following example, in which the minor components in a blend of $C_6$, $C_7$, and $C_8$ aromatics had to be estimated.

Each of the components was injected singly into a column operated at what was expected from past experience to be suitable conditions of temperature, pressure, and carrier gas (nitrogen) flow rate and the retention volumes measured. By inspection of the traces obtained the choice of a volatile liquid for use as an internal standard was provisionally decided and confirmed by injection of a suitable volume into the column for determination of its retention volume. The use of an internal standard serves a dual purpose. The concentration of a component of a mixture may be determined by measurement of the area contained by

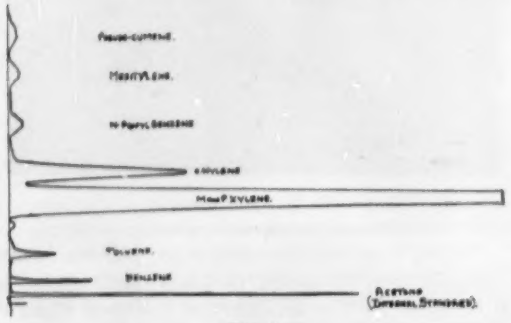



FIG 4

AROMATIC SEPARATION

the elution peak on the recorder trace. By adding to both sample and synthetic mixtures a similar and known amount of a suitable volatile substance, the concentration of all components of the sample may be referred to this known concentration. Slight variations in operating conditions affect sample and internal standard alike, and some relaxation in conditions may be allowed without appreciable error. To complete the calibration a series of known mixtures is prepared and a known and fixed amount of the selected internal standard is added to each. Calibration curves are then prepared showing for each component the relation between concentration and the ratio of component peak area–standard peak area. It has been found in practice that if the height of the elution peaks is substituted for the areas there is little effect on accuracy.

The sample is injected on to the column through the rubber serum cap by means of a micrometer syringe, a method introduced by Ray.[20] The sample is vaporized immediately by a small auxiliary heater wound on the column below the point of entry of carrier gas. This heater is necessary for clear-cut separations

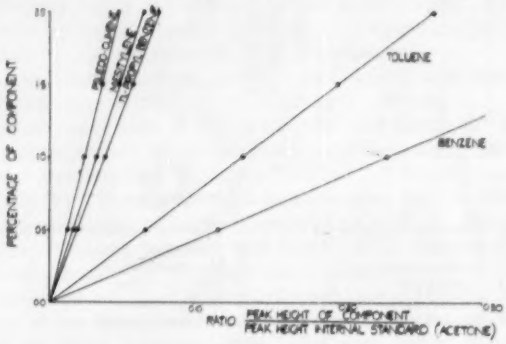



FIG 5

CALIBRATION CURVES

which are achieved only if the sample is absorbed on the top of the column as rapidly as possible. The components are eluted from the column singly, each component giving rise to an elution peak.

Fig 4 shows the trace obtained from this mixture of $C_8$ aromatics containing 0·5 per cent each of benzene, toluene, mesitylene, and pseudo-cumene. The column packing consisted of graded "Celite" impregnated with 30 per cent by weight of dinonylphthalate [di-(3,5,5-trimethylhexyl) phthalate]. Fig 5 shows the calibration curves, and the following table gives the results :

TABLE I

| | % by weight | | | | | |
|---|---|---|---|---|---|---|
| | Found | Present | Found | Present | Found | Present |
| Benzene . . | 0·55 | 0·53 | 0·98 | 0·95 | 1·40 | 1·45 |
| Toluene . . | 0·38 | 0·40 | 0·97 | 1·00 | 1·52 | 1·56 |
| *n*-Propyl benzene . | 0·31 | 0·31 | 0·72 | 0·75 | 1·05 | 1·02 |
| *pseudo*Cumene . | 0·33 | 0·35 | 0·75 | 0·72 | 0·95 | 0·92 |
| Mesitylene . . | 0·29 | 0·31 | 0·69 | 0·70 | 1·00 | 0·97 |

## ANALYSIS OF PETROLEUM FRACTION

One of the more complicated analyses so far attempted was that of a petroleum fraction of unknown origin whose distillation curve corresponded roughly to a gasoline with I.B.P. of 50° C, 5 per cent 66·5° C, 95 per cent 124·5° C, and F.B.P. 146° C. A preliminary liquid-phase separation was carried out on a 10-ml sample through a silica gel column, dividing the sample into aromatic and saturated groups. 0·05 ml portions of each of these two fractions and of the original mixture were then analysed separately on a

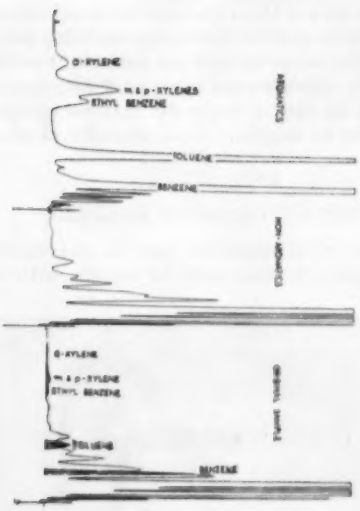



FIG 6

TRACES OF ORIGINAL GASOLINE SAMPLE AND OF AROMATIC AND NON-AROMATIC FRACTIONS

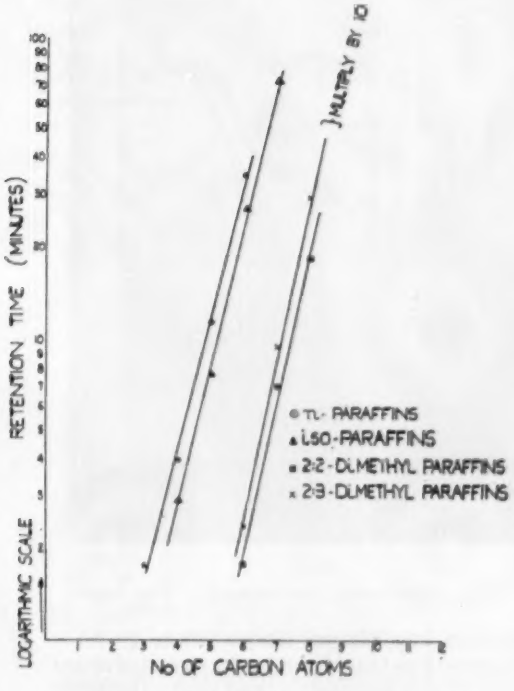



FIG 8

LOGARITHMIC PLOT OF COMPONENTS

FIG 7

GASOLINE RUN ON LARGE COLUMN

vapour-phase partition column similar to that described above. The three chromatograms are shown in Fig 6. The aromatic fraction trace shows a small proportion of low-boiling non-aromatic material followed by a series of easily identifiable aromatic components. Comparison of the three traces enables sixteen major components to be picked out immediately in the chromatogram of the original mixture, and in addition to the known aromatic peaks, a number of the non-aromatic peaks can be identified as components of known chromatographic characteristics, or as composite peaks, grouped by molecular weight.

Further identification of the minor non-aromatic components required more detailed separation, which was achieved by chromatographic fractionation. For this purpose a larger vapour-phase column was used, measuring 6 ft × ½ inch dia, and capable of dealing with a 0·5-ml sample, *i.e.* ten times the size of the sample normally used. The exit gas system of this column was fitted with cooled U-tube fraction collectors isolated as required by taps. The operating conditions were similar to those used for the primary analyses, except that the temperature was decreased to give higher resolution. A complete chromatogram of the non-aromatic fraction of the sample obtained in these conditions is shown in Fig 7. The peaks were taken off successively as separate fractions, which

TABLE II

| Frac. No. | Non-aromatic | B.p. | Frac. No. | Aromatic | B.p. | Retention time, in mins |
|---|---|---|---|---|---|---|
| 1 | Propane | −42 | | | | 1·8 |
| 2 | *iso*Butane | −12 | | | | 2·6 |
| 3 | *n*-Butane | − 0·5 | | | | 3·8 |
| 4 | *iso*Pentane | 27·9 | | | | 8·0 |
| 5 | *n*-Pentane | 36·1 | | | | 11·0 |
| 6 | 2,2-Dimethylbutane | 49·7 | | | | 18·0 |
| 7 | 2,3-Dimethylbutane / 2-Methylpentane | 58·0 | | | | 24·0 |
| 8 | *n*-Hexane | 68·7 | | | | 35·0 |
| 9 | 2,2-Dimethylpentane | 79·1 | | | | |
| 9 | 2,4-Dimethylpentane | 80·5 | | | | |
| 10 | *cyclo*Hexane | 80·8 | | | | |
| 10, 11 | 1,3-Dimethyl*cyclo*pentane | 91·5 | | | | 63 to 84 |
| 10, 11 | 2,3-Dimethylpentane | 89·7 | | | | |
| 11, 12 | 2-Me-hexane | 89·7 | | | | |
| 11, 12 | 3-Me-hexane | 91·8 | | | | |
| 13 | *n*-Heptane | 98·4 | | | | 110 |
| | | | 1 | Benzene | 80·1 | 114 |
| 14 | Methyl*cyclo*hexane | 100·0 | | | | 140 |
| 15 | 1-Methylethyl*cyclo*pentane | 121·0 | | | | 160 |
| | 2,5-Dimethylhexane | 108·2 | | | | |
| | 1,2,4-Trimethyl *cyclo*pentane | 117 | | | | |
| | 2,4-Dimethylhexane | 110·2 | | | | |
| 16 | 2,3,5-Trimethylhexane | 124° C | | | | 200 |
| | 2,2,3,4-Tetramethylpentane | 133° C | | | | |
| | 1,3,5-Trimethyl*cyclo*hexane | 138° C | | | | |
| | | | 2 | Toluene | 110·6 | 360 |
| | | | 3 | Ethyl benzene | 136 | 360 |
| | | | | *m*-Xylene | 139 | |
| | | | | *p*-Xylene | 138 | |
| | | | 4 | *o*-Xylene | 144 | |

were then analysed mass-spectrometrically, and as Table II shows, a total of thirty-two components was finally identified.

From the appropriate retention volumes listed above, Fig 8 has been plotted, showing the appreciable effect of isomeric structure on retention volumes. When sufficient data of this type has been accumulated, and methods developed for increasing resolving power for the higher molecular weight components, it will be possible to carry out complete analysis of complicated mixtures, such as this, entirely by chromatography, without recourse to auxiliary methods, such as mass-spectrometry.

## ANALYSIS OF GASEOUS SAMPLES

The arrangement of apparatus used for gas analysis is generally similar to that used for liquids, with the simplification that the gas sample (10 to 20 cc) is merely carried into the column by the stream of eluant gas from a by-pass gas pipette. Gas analysis is readily adapted to automatic repetition, and one form of apparatus developed for this purpose for operation on a plant gas stream is shown in Fig 9.

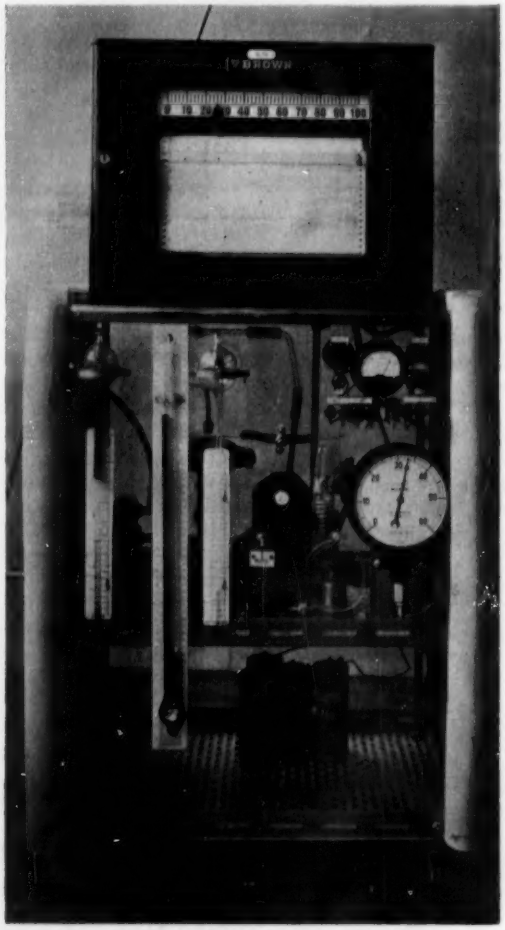



FIG 9
AUTOMATIC GAS APPARATUS

## GAS ANALYSIS

Gas columns are conveniently operated at room temperature, and the inlet pressure of the nitrogen is kept at 25 p.s.i. A large number of high-boiling

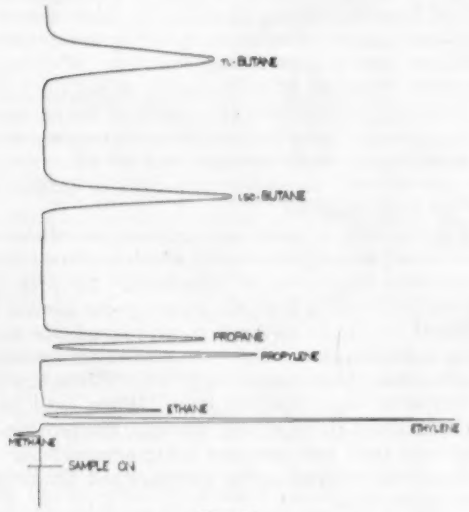



FIG 10

TRI-*ISO*BUTYLENE SEPARATION OF HYDROCARBONS

liquids have been tried as the stationary phase, and several have been found to be of special use. *iso*-Butylene trimer, formed by cold acid polymerization, is a mixture of several hydrocarbons boiling in the range 190°–200° C; hydrocarbon gases are eluted from this liquid in order of their boiling points and, presumably, the forces of solubility involved are van der Waal's forces only. Separation of a mixture of hydrocarbons on a 6-ft column containing kieselguhr impregnated with 30 per cent by weight of this tri-*iso*-butylene is shown in Fig 10. This substance is not suitable for the separation of the isomers of *n*-butylene from butadiene because of the proximity of their boiling points. By the use of a polar liquid as the stationary phase, hydrogen bonding between the electro-negative groups of the liquid and the activated hydrogen atoms of the unsaturated hydrocarbon is brought into play, and it is possible to achieve a partial separation of such mixtures. The diketone acetonyl acetone is one of the most efficient polar substances for such separations. Fig 11 shows the analysis of a $C_4$ cut for butadiene on a 6-ft column impregnated with acetonyl acetone at 20° C. A particular point of interest is the partial separation of *cis*- and *trans*-butene-2, whose boiling points differ by less than 2° C; these two substances may, however, be completely separated at 0° C. This figure also shows the type of record produced by the automatic apparatus; the time cycle is 30 minutes.

It is also possible to make use of the forces of attraction between metal ions and unsaturated hydrocarbons to achieve special separations. These forces are often of a higher order of magnitude than hydrogen bonds, and are likely to be more specific due to steric effects. A saturated solution of silver nitrate in glycol has been used with some success. Table III shows a comparison of the retention volumes (the retention × flow

TABLE III

*Retention Volumes of Some Hydrocarbons on a 6-ft Column Containing 30 per cent wt of Tri-isobutylene (I), Acetonyl Acetone (II), and a Saturated Solution of Silver Nitrate in Glycol (III). Inlet Pressure 25 p.s.i., Flow Rate 2·0 Litres/hour, Temperature 20° C*

| Hydrocarbon | Retention volume; ethylene = 1 | | |
|---|---|---|---|
| | Column I | Column II | Column III |
| Methane | 0·8 | 0·7 | 0·75 |
| Acetylene | 0·95 | 3·8 | — |
| Ethylene | 1·0 | 1·0 | 1·0 |
| Ethane | 1·2 | 1·0 | 0·75 |
| Propylene | 2·4 | 2·2 | 1·0 |
| Propane | 2·7 | 1·5 | 0·75 |
| Methyl acetylene | 2·85 | 11·5 | — |
| *iso*Butane | 5·6 | 2·2 | 0·75 |
| *n*-Butane | 7·5 | 3·0 | 0·75 |
| Butadiene | 6·7 | 10·0 | 10·0 |
| Butene-1 | 6·7 | 4·75 | 6·25 |
| *iso*Butene | 6·7 | 4·75 | 3·25 |
| *Cis*-butene-2 | 8·0 | 5·85 | 1·75 |
| *Trans*-butene-2 | 8·9 | 6·8 | 5·5 |

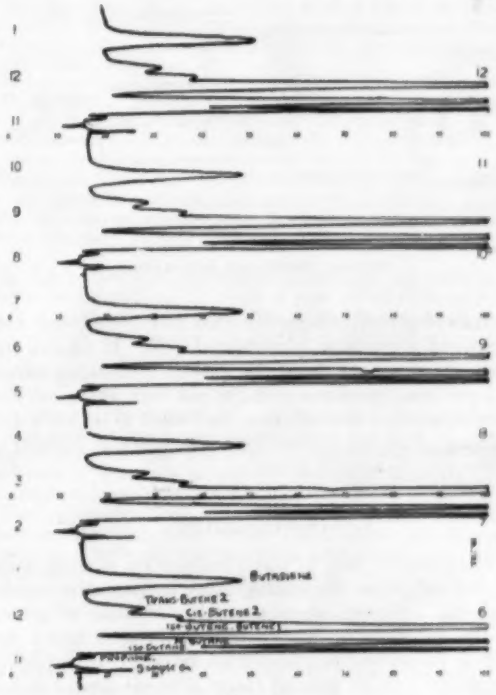



FIG 11

$C_4$ CUT

rate) of a number of hydrocarbons in the three liquids described.

A particular use for a column containing silver is the analysis of traces of ethane in ethylene. These substances are not separated on acetonyl acetone, where hydrogen bonding is not strong enough to reverse their respective volatilities. On tri-*iso*butylene ethane is eluted after ethylene, and if present in trace amounts only will not be completely separated from the trailing peak of a large quantity of ethylene. On a column containing 30 per cent of a saturated solution of silver

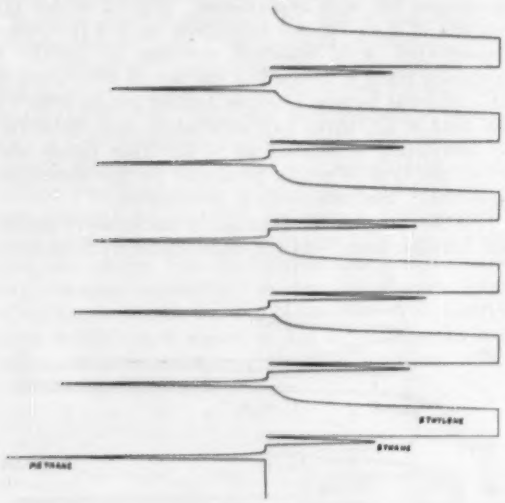


Fig 12

ETHANE ETHYLENE SEPARATION

nitrate in glycol, ethane is eluted before ethylene, and complete separation is obtained. Fig 12 shows the analysis of an ethylene gas stream containing about 0·5 per cent methane and 2·0 per cent ethane. For this separation two columns were used in series, a 4-ft column of tri-*iso*butylene followed by a 6-ft column of silver nitrate–glycol solution.

## CONCLUSION

Emphasis is laid in the foregoing on current work in vapour-phase chromatography because the results recently achieved show it to be capable of giving analytical data on hydrocarbon mixtures which are better in several respects than those given by other methods. In its present stage of development it has considerable advantages in speed and resolving power for components in the lower molecular weight range. Upward extension of the effective molecular-weight range is an objective which can be approached in several ways, and work is being done on this aspect. Increase of resolving power is necessary to deal with more complex mixtures, and to achieve this, more detailed knowledge is required of the effects of variations in the composition of the stationary phase solvent. This paper deals only with the analysis of hydrocarbon mixtures, but the vapour-phase partition method has very wide applicability to other classes of compounds, and information is being accumulated which will lead to general improvements. Compared with other methods of fractionation, it has the merit of indicating continuously the purity of the fractions as they emerge, since the peak shape is very sensitive to overlapping of components and no phenomenon comparable with azeotrope formation in distillation has yet been observed.

It is too early to make any general deductions on the accuracy and reproducibility which can be attained in different conditions of operation. As with all physical methods of analysis, accuracy can always be increased by closer calibration with synthetic mixtures, and when this is done, the results are certainly as accurate as those attainable by other methods, such as optical or mass spectrometry. When used as a routine method on repetition analysis, the problem is a different one, and data are being accumulated on performances studied under standardized conditions over long periods.

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## DISCUSSION

**H. Rampton :** I think I am right in saying that this is the first paper presented to the Institute on the subject of chromatography, and we in the petroleum industry must remember that the I.C.I. do not derive the whole of their livelihood from hydrocarbons, so I think we owe them a special debt of gratitude for presenting this paper this evening. I think that the title of the paper is a trifle misleading, since 90 per cent of it deals with one particular aspect, namely that of gas chromatography.

The art of chromotography has progressed far since the original experiments of Tswett on plant pigments, and while the name was most apt then, there is much to commend the use of the term "Selective Adsorption" now. In fact, as you have seen already, the development of colour in certain chromatographic separations has to be assisted artificially by the addition of visual markers or indicators. In this connexion, I would like to have seen reference made in the paper to the work of Conrad, Criddle, and Le Tourneau which has led to the development of the well-known ASTM fluorescent dye indicator (FIA) method for hydrocarbon type analysis.

To return to the main subject of the paper, *i.e.* gas chromatography, there is no doubt that it is an analytical tool of great promise and possibilities. Its application to the analysis of gas streams is attractive, not only on account of the small size of sample required and simplicity of operation, but also from the point of view of capital outlay. A mass spectrometer, to perform the same service with its ancillary calculating equipment, costs from six to ten times as much, and will also demand a high degree of specialized operational skill and expert maintenance. On the other hand, it is quite possible that these two instruments can be made to work together to give an even greater precision, and I have in mind, as Dr Bradford confessed tonight, they had to cheat by taking the fraction from the gas chromatographic column, and do some more analyses of those peaks by the mass spectrometer, and I can foresee developments there in that connexion. The usefulness of gas chromatography is well illustrated by the examples quoted in the paper, and these will serve, in all probability, as an *apéritif* to whet the appetities of experimenters who may be having their first introduction this evening to this comparatively new technique.

There are a number of points which I would like to raise with the authors of this paper.

(1) There appears to be a discrepancy between Fig 4, Table I, and the actual script. A mixture of $C_8$ aromatics containing 0·5 per cent each of other aromatics is indicated. Percentages other than 0·5 per cent are quoted, presumably because more than one blend was tested. If ethylbenzene was present, where would the corresponding peak occur ?

(2) Would it not be advantageous to set out the compounds detailed in Table III in strict order of boiling point, possibly giving the actual figures for ease of reference?

(3) The graph in Fig 12, depicting the separation of methane and ethane from ethylene, is striking, but no explanation is given of the reason for the opposite signs of the deflections for methane and ethane, presumably due to the differences in thermal conductivity of these hydrocarbons compared with that of the reference gas stream.

**Dr B. W. Bradford :** The order in which the hydrocarbons are listed in Table III is, with the exception of *n*-butane, the order of elution from a trimer column, which is not quite the same as the order of boiling points. Your explanation for the opposite signs of the methane and ethane peaks in Fig 12 is the correct one.

**D. Harvey :** Fig 4 is intended to serve merely as an example of the type of curve obtained, and is actually one of the runs obtained in the preparation of the calibration curves illustrated in Fig 5.

In general (although there are exceptions), the members of any homologous series emerge from the column in order of ascending boiling point, and ethyl benzene if present would be eluted before the combined *m*- and *p*-xylene peak.

**K. H. V. French :** I would like to make one or two points about the gasoline that Dr Bradford analysed. He showed us that a considerably better separation of the components could be obtained by preliminary separation of the aromatics and non-aromatics. Now, the sample of gasoline used was unusual in that it apparently contained no olefins. Has Dr Bradford and his colleagues handled similar materials that contained aromatic, saturated, and unsaturated hydrocarbons. What advice can he give us as to what preliminary separations would be necessary with such materials?

**Dr B. W. Bradford :** The answer is no, we have not made a study of this subject, and although I have no doubt it would be quite easy to find what the right sort of pre-treatment is, we have not tried a whole series of different types of gasoline so I cannot offer you anything further. Perhaps, however, Mr Harvey may have something to add.

**D. Harvey :** Olefins, as such, present no more difficulty than paraffins or aromatics. Their presence in a gasoline would, however, increase the complexity of the mixture, and some pre-treatment would be necessary. Segregation of the three groups is, however, quite feasible on the specially selected silica gels available today, and, although such separation may not be complete, it should prove sufficient for this purpose.

**L. Kin :** None of the common solvents can truly be said to be immobile. In view of this, to what extent is the loss of the immobile phase a factor in determining : (*a*) the life of the column ; (*b*) the life of the katharometer (which will have solvent deposited on it if it is not heated to a temperature at least equal to that of the column) ?

In the analysis of a sample of mixed xylenes, figures are quoted to the second place of decimals. An accuracy of this order would entail very exact reading of peak heights and, for the low concentrations reported, the thickness of the trace would be very important. Have you any comments on this ?

The calibration curves shown cover small concentrations of minor components only. Does the linear relationship between percentage of component and peak height ratio continue into higher concentrations, and is it possible to determine the concentration of major components by vapour-phase chromatography ?

**Dr B. W. Bradford :** I ought to have said that the katharometer is heated. It must be heated, of course, to prevent condensation, since columns can be operated for several months without change.

I have no doubt that liquid is slowly lost, but very slowly indeed, and the concentration in the gas stream is such that it does not affect our detector.

The maximum temperature of operation is very interesting. So far as I know, no one has operated at a higher temperature than 300° C, and that is difficult. It is probably possible to operate at 200° C without much more difficulty than with the apparatus here which is operating at a little over 100° C. This is a major point in the development of vapour-phase chromatography ;

in order to obtain an extension to higher molecular weight material one must be able to work at a higher temperature.

You commented on the figures for the aromatics analysis. I can only say that this is an extract from a much larger investigation, and I could have given you far more figures, but I did not think they were relevant because the object of this paper was not to show you what the analytical accuracy of this method is in routine operations. We have not established that yet. We have only attempted to show you how the method operates and give you some of the results, and those, as I said, have been obtained under carefully calibrated conditions, which, I think, represent the best we can expect at the moment.

I do not think that the criticism about the thickness of the trace is a very real one. Several factors enter into this, as everyone who has used infra-red or other methods depending upon traces knows: there is a noise level, there is the thickness of the line, and so on, but experience and careful calibration enable you to get fairly close to the actual deflection from zero if your apparatus is working correctly. You asked if the method can be used for higher concentration. We do carry the calibration curves higher: we have not shown them in this particular case, but it is possible.

**D. Harvey:** In answer to Mr Kin's query on the extension of calibration curves to higher concentrations we have found at Billingham that the linear relationship between percentage of component and peak height ratio does indeed hold up to the highest concentrations, if due precautions are observed and the columns are not overloaded. To determine the concentration of major components one must reduce the sensitivity of the katharometer or introduce an attenuator into the recorder circuit.

In regard to accuracy we have found in the performance of some two-hundred to three-hundred determinations per month over the past two years on a wide variety of substances that our accuracy rarely falls below $\pm 3$ per cent and is usually much better than this.

**M. Scott Archer:** I have two questions.

First, would Dr Bradford explain whether there was any variation in the degree of asymmetry of the spectrum in vapour-phase chromatography with the lengths of time in the column, and also whether allowance is made for this asymmetry in quantitative estimation from peak heights?

Secondly, I presume that the 3 per cent accuracy claimed in a reply to a previous question is 3 per cent on each component measured, not on the total material present.

**Dr B. W. Bradford:** The 3 per cent is, of course, on each component present, and I am sorry we did not make this clear.

**D. Harvey:** In quantitative work every precaution is taken to perform calibration and sample runs under identical conditions, and consequently any departure from asymmetry would appear in both traces. In practice, however, if the conditions of temperature, flow rate, etc., are well chosen the departure from asymmetry is slight, and presents no problem. In all cases we find that a measurement of peak height provides satisfactory accuracy.

**R. R. Wilson:** Have the authors had any experience of attempting the separation of the two isomers of commercial di-*iso*butylene and tri-*iso*butylene in their apparatus?

Secondly, have they any experience of the separation of carbonyl compounds?

**D. Harvey:** We have not attempted the separation of either of the polymers mentioned. We have, however, had a look at the tetramer, and in this case we were able to distinguish four peaks. We isolated some of the material under each peak and submitted this for ultraviolet examination but obtained little further information.

We experience no difficulty whatever in the separation of carbonyl compounds with the possible exception of formaldehyde. Here we find that the Celite behaves as an excellent polymerization catalyst, but we have had some success by substituting silver sand for the Celite.

**Dr D. P. Young:** There are two opposing schools of thought in gas-phase chromatography. One uses horizontal tubes, and the other vertical tubes. An earlier communication from I.C.I. describes the use of horizontal tubes, but I notice our speakers tonight prefer to use vertical tubes. I wonder if they have any reason for it apart from the obvious one of compactness?

**Dr B. W. Bradford:** Only compactness, and because we believe it is more easily arranged.

**G. C. Eltenton:** Using nitrogen, it appears that the methane peak registers in the "negative" direction, while all other peaks register in the "positive" direction. Would it not be possible to overcome this difficulty by using hydrogen as the carrier? And would not the overall sensitivity (signal–noise ratio) be considerably enhanced?

Secondly, have you found a means of introducing liquid samples with a robot sampler suitable for plant use? I should imagine this would be very difficult if memory effects in the sample lines are to be avoided. Would it be better to flash vaporize all liquid samples and use the robot sampler designed for vapours?

**Dr B. W. Bradford:** On the second of Dr Eltenton's points, we have not yet succeeded in building a really satisfactory liquid sampler. We have only used the automatic sampler for gases. The problem of taking 0·05 ml of a liquid is a fairly difficult one, which we have not solved yet. We have done some work on flash vaporization of certain types of samples: I think that is possibly a line to be followed.

**D. E. Chalkley:** Mr Eltenton is quite right in assuming that the use of hydrogen as a carrier gas would give all peaks in the same direction. At the same time the signal to noise ratio is increased by a factor of about 50 if the katharometer wires are heated to the same temperature as they are in nitrogen. There are two known disadvantages. One is that the separation is slightly worse, due to the high rate of diffusion of the hydrogen molecules. The other is that silver nitrate columns are rapidly reduced by hydrogen at room temperature.

**D. H. Desty:** It seems a pity that Dr Bradford failed to mention in the discussion of liquid chromatography the two procedures of liquid reversed-phase partition chromatography and the gradient elution technique on solid adsorbents. They have both been described, and should be of great use in the separation of higher molecular weight hydrocarbons.

In connexion with gas chromatography, I think Dr Bradford has been a little hard on the displacement procedure. It seems a pity to condemn the method merely because of the deficiencies of the detector he is using. The method can be made extremely accurate by using very low concentrations of the developer, and the appearance of elution peaks may be prevented by increasing the activity of the absorbent. Quantitative measurements are independent of the characteristics of the detector

and recorder system, depending on a simple time determination.

In connexion with the elution procedure I have always been curious why our friends at I.C.I. use sub-atmospheric pressure with their apparatus for volatile liquid analysis. It is possible that the rubber serum cap necessitates this, but it is even more difficult to understand why elevated pressures are used with the gas analysis apparatus. This increase in pressure should not affect the retention volumes, as these are dependent on the partition coefficient only, and should not significantly reduce longitudinal diffusion. It seems therefore an unnecessary complication.

I think one of the most important points in Dr Bradford's paper is the application of complex formations to gas chromatography. The steric effects shown by the butene isomers on the silver nitrate–glycerol stationary phase are very interesting, and these might well be more pronounced among the higher molecular weight olefins.

One question I should like to ask in connexion with Table III is whether the data given are corrected for the dead volume of the column and what is the ratio of retention volumes of ethylene determined in the three stationary phases?

**D. E. Chalkley:** We have found that a high pressure of carrier gas is advantageous for the more difficult gas separations, *e.g.* of ethane and ethylene at room temperature. As Mr Desty says, the partition coefficient, and therefore the retention volume of a substance, should be independent of the partial pressure of the carrier gas, and the increase of efficiency we have observed at high pressures is probably due to a diffusion effect.

The retention volumes in Table III are not corrected for the dead volume of the column, and are included for comparison purposes only.

**W. A. Wiseman:** In the case of a liquid separation, does the liquid vaporize at once, or is there a distinct time that it takes to vaporize, and if so, does it have an effect on the shape of the peaks?

**Dr B. W. Bradford:** We use a heater at the top of the column to ensure an almost instantaneous vaporization.

**W. A. Wiseman:** Concerning different-sized columns, can you give any idea as to how you judge their capacity?

**Dr B. W. Bradford:** We continue to add larger quantities until it is clear that the limit is reached; this is often indicated by peak distortion or change of a peak's position.

**L. Kin:** Have you had experience with detector analysis other than a katharometer?

**Dr B. W. Bradford:** Several people are working on that and have worked on it. Certainly, it would be an advantage to have a more sensitive detector than the katharometer. Although I showed you that it is, in terms of micrograms, highly sensitive, it does not, in fact, easily go down to parts per million in a mixture, but it is very hard to beat for analytical work. It is so stable and robust. If we could find something which was more sensitive but which was also stable and robust, then it would be a great advantage. It would enable us to push up the temperature of operation, work with higher molecular weight materials, and deal better with traces.

**W. A. Wiseman:** Have you had any trouble with water, and if so, how do you remove it?

**D. Harvey:** We do not remove it; we inject the sample as received having chosen a static liquid phase over which water has a high retention value. For aqueous alcoholic solutions we have made use of glycerol, and for aqueous amine mixtures we have used tri-ethanolamine. We have also used combined columns operated in series containing, for instance, glycerol in the first leg and di-nonyl phthalate in the second.

**W. A. Wiseman:** What happens if you are dealing with compounds with a high boiling point?

**D. Harvey:** Certainly that is very difficult. It may be possible in such cases to arrange for the water to be eluted first, thus avoiding interference. Each case would require to be considered on its merits.

**R. B. Southall:** There are probably many more questions to be asked, but as statistically we are just two-thirds of the way through the evening, it would be in keeping if I said thank you to the authors now, as we probably will not be keeping in our seats during the demonstration which will complete the evening.

In my view, this is the type of paper that the Institute welcomes. In many respects it is original, although it is related to work going on elsewhere; and I think that Dr Bradford and his colleagues, Mr Harvey and Mr Chalkley, are to be congratulated for the work they have done already, which led up to this paper, and for putting it forward in such an interesting form. Dr Bradford, Mr Harvey, and Mr Chalkley, we would like you to accept the thanks of this meeting for the contribution you have made to the Institute's proceedings.

The vote of thanks was accorded with acclamation.

# CORRELATION BETWEEN EQUILIBRIUM FLASH VAPORIZATION AND ASTM DISTILLATION DATA OF PETROLEUM MIXTURES*

By J. C. CHU† and E. J. STAFFEL†‡

SUMMARY

In the design and performance prediction of petroleum processing equipments, the correlation between equilibrium flash vaporization and ASTM distillation data has been frequently used as an essential tool. The correlations proposed so far have not been entirely satisfactory. Discrepancies between the plant data and the results calculated from the existing correlations have been frequently encountered by practising engineers. This work was undertaken to investigate the existing correlations and to develop an improved one to be used in petroleum refining engineering.

Since the experimental data in the published literature are very limited, the data recently contributed by nine major oil companies have constituted the bulk of data compilation for 151 systems. Only sixty-five sets of data were used in developing the correlation; the remaining sets are either incomplete or eliminated because of indication of cracking during the distillation. Starting with the atmospheric ASTM curve, several variables were investigated, including characterization factor, slope ratio, average molecular weight, and various slopes of ASTM distillation curves. The correlation finally developed consists of an improved method in predicting the 50 per cent equilibrium flash vaporization (EFV) from 50 per cent ASTM point with characterization factor, and 10–70 per cent ASTM slope as additional variables. The slope of EFV at different percentages of vaporization are related to those of ASTM in the same way as suggested by Edmister and Pollack.[7] However, the graph has been modified in the light of sixty-five sets of consistent data.

The present correlation, as well as the previous ones, was checked with additional experimental data. For the 50 per cent correlation the arithmetic average error is −12·5° F and mean deviation ±13·5° F. This represents an improvement over the existing methods ranging from 40 to 110 per cent. The improvement of similar order of magnitude is obtained at the other points.

## INTRODUCTION

In the design and performance prediction of petroleum processing equipment it is essential to have vapour–liquid phase equilibrium data or flash equilibrium data. Many stills have been developed to perform flash vaporization equilibrium studies.[8, 12, 19, 28, 32] However, the laboratory determination requires a considerable amount of time to attain equilibrium. Ten Eyck [32] reported ¾ hr to 4 hr to reach equilibrium for a recirculating type still. In the continuous type still 3 to 6 hr were required.[8] In a later paper Edmister reports 8 to 10 hr to bring the still up to any desired temperature, and 3 hr maintaining steady conditions. As there are at least 6 or 7 points required for the determination of the complete flash curve, it can be seen that these laboratory methods would require tremendous amounts of time. In addition, the units require 1 to 2 brl of sample and must be operated by skilled technicians. There are also many controls and instruments, and the initial cost is high.

In view of the above mentioned difficulties in laboratory determinations, use has been made of correlations, developed to estimate equilibrium flash vaporization (EFV) data from ASTM distillation data which are easily and readily determined.[4–7, 10, 13–17, 19, 32, 37]

The two methods being most widely used are those of Edmister and Pollock [7] and Maxwell.[13] The Maxwell method is a modification of the Packie method.[19] In the Nelson and Harvey method [15] the flash curve is assumed to be a straight line. As the flash curve exhibits a certain amount of curvature, this third method is an approximation only. The method of Okamoto and van Winkle [17] shows a straight line relationship between the percentage off of EFV and the percentage off of ASTM, and does not consider the effect of the ASTM slope.

The Maxwell method does make a correction for curvature. His correction, however, is merely an average value of deviations. Maxwell asserted the correction ratio always positive. In about 25 per cent of the samples used in this paper, this ratio was found negative. Edmister's method makes a curvature correction and appears to be more convenient. Although the relationship between 50 per cent ASTM and 50 per cent EFV was reported as a straight line, a curve may give better fit to the relationship. The various terms of deviation presented in Table I are defined as follows:

The difference between predicted values and experimental values was determined without regard to sign. This difference was totalled for all the samples and the total divided by the number of samples gives the average arithmetical error.[3] Average algebraic error is the same as above except that differences were determined with regard to sign. The predicted value minus the experimental value gives the algebraic difference. Average mean deviation equals the sum of the actual deviation minus the average algebraic deviation for all of the samples, divided by the total number of samples. Standard deviation equals the square root of the sum of the squares of the actual deviation minus the average algebraic deviation for all the samples divided by the total number of samples.[9]

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TABLE I

*Error Comparison—All Methods*

| | Arith. avg. | Alg. avg. | Mean dev. | Std. dev. |
|---|---|---|---|---|
| 10% point : | | | | |
| Okamoto and van Winkle | ±39·7 | −31·4 | 26·3 | 39·3 |
| Maxwell | ±17·95 | − 8·8 | 17·80 | 28·8 |
| Maxwell mod. without "K" | ±15·60 | − 3·62 | 16·45 | 27·1 |
| Maxwell mod. with "K" | ±17·05 | − 0·19 | 17·05 | 27·3 |
| Edmister | ±21·20 | − 6·91 | 21·0 | 32·7 |
| Edmister mod. without "K" | ±17·95 | − 7·87 | 17·67 | 29·6 |
| Edmister mod. with "K" | ±17·80 | − 3·18 | 18·10 | 26·6 |
| 30% point : | | | | |
| Okamoto and van Winkle | ±20·8 | − 4·18 | 20·8 | 30·3 |
| Maxwell | ±16·46 | − 8·80 | 15·94 | 26·3 |
| Maxwell mod. without "K" | ±15·56 | − 6·01 | 15·5 | 24·0 |
| Maxwell mod. with "K" | ±14·86 | − 2·58 | 15·3 | 25·7 |
| Edmister | ±16·95 | − 4·97 | 18·0 | 27·4 |
| Edmister mod. without "K" | ±15·95 | − 4·68 | 16·08 | 25·0 |
| Edmister mod. with "K" | ±14·85 | − 2·28 | 15·13 | 23·9 |
| 50% point : | | | | |
| Okamoto and van Winkle | ±28·2 | +19·0 | 20·9 | 27·4 |
| Maxwell | ±19·0 | − 0·29 | 19·0 | 29·8 |
| Edmister | ±16·76 | − 1·35 | 16·95 | 24·8 |
| Edmister mod. without "K" | ±15·90 | − 0·94 | 15·95 | 23·45 |
| Edmister mod. with "K" | ±12·48 | − 4·40 | 13·80 | 19·50 |
| 70% point : | | | | |
| Okamoto and van Winkle | ±46·3 | +44·5 | 28·0 | 35·3 |
| Maxwell | ±20·64 | + 4·44 | 20·7 | 29·1 |
| Maxwell mod. without "K" | ±15·39 | + 0·72 | 15·35 | 22·3 |
| Maxwell mod. with "K" | ±15·80 | + 4·12 | 15·90 | 22·0 |
| Edmister | ±16·70 | − 0·18 | 18·0 | 25·7 |
| Edmister mod. without "K" | ±15·20 | − 0·70 | 15·20 | 21·4 |
| Edmister mod. with "K" | ±16·67 | + 2·96 | 17·00 | 22·7 |

The success of an empirical correlation depends, to a large extent, upon the extensiveness of the data employed for its development. The accuracy of the data assures the right statistical average, and increases the utility of the resulting correlation. In view of the discrepancy frequently encountered between plant data and results calculated from the existing correlation, this work was undertaken to develop an improved correlation. In addition to the existing data in the published literature, a considerable amount of unpublished data were obtained from nine major oil companies. Among data on 151 samples collected, sixty-five sets of data were selected for this work. Screening of the data was based upon the following requirements :

(1) The data should be complete by themselves. 50 per cent points on EFV curve ; API gravity ; 10 per cent ASTM, and 70 per cent ASTM points which were employed in the correlation had to be available.

(2) The ASTM curve must be free from any evidences of cracking. According to the specification of ASTM distillation, "cracking will be evidenced by an increase in distillation rate with a thermometer reading that may advance very slowly, remain stationary, or recede, and an effort to adjust the distilling rate will usually result in a decided drop in the temperature reading." [1] In screening the data with regard to cracking, the data were graphically presented for a careful scrutiny to select the data with little evidence in cracking. The presence of cracking in the later stage of distillation can be detected by the slope of the distillation curve. The experimental data were not extrapolated because of the inaccuracies involved, especially at the initial boiling point and end point.

The present work is limited to the correlation under atmospheric pressure. For the benefit of those interested in the statisical basis of correlation, sixty-six sets of experimental data, which were selected and employed as the basis for the present correlation, are given in Table II. The other set of data is presented elsewhere.[2, 7, 10, 18, 20, 21, 23-27, 29-31, 33, 34]

The ASTM distillation data were obtained in accordance with D86–46 and D158–41 of Standards of ASTM. Method D86–46 was prepared to be used for gasoline and similar petroleum products. The reproducibility is ±6° F for the initial boiling point and the end point. The reproducibility should not exceed the differences in temperature readings over 2 ml of distillate at the point in question. Method D158–41

TABLE II

*Atmospheric ASTM and EFV Distillation Data*

| Description | Saginaw crude | Treated press. dist. | Naph. btms. 25·4°% of No. 18 | Press. dist. | Naph. btms. 68°% of No. 20 |
|---|---|---|---|---|---|
| Sample no.[7] | 17 | 18 | 19 | 20 | 21 |
| °API | 44·3 | 52·3 | 39·3 | 50·8 | 44·2 |
| ASTM : | | | | | |
| I.B.P. | 116 | 65 | 276 | 80 | 170 |
| 10% | 187 | 141 | 355 | 165 | 258 |
| 20% | 243 | 200 | 385 | 218 | 303 |
| 30% | 293 | 244 | 405 | 258 | 327 |
| 40% | 346 | 282 | 419 | 291 | 353 |
| 50% | 409 | 317 | 430 | 321 | 370 |
| 60% | 475 | 348 | 441 | 353 | 388 |
| 70% | 550 | 378 | 452 | 382 | 406 |
| 80% | 644 | 402 | 467 | 405 | 424 |
| 90% | — | 439 | 505 | 433 | 443 |
| E.P. | — | 493 | 561 | 500 | 500 |
| EFV : | | | | | |
| B.p. | — | 137 | 334 | 122 | 260 |
| 10% | 234 | 175 | 385 | 191 | 300 |
| 20% | 275 | 209 | 406 | 228 | 320 |
| 30% | 307 | 237 | 415 | 254 | 334 |
| 40% | 341 | 263 | 422 | 274 | 345 |
| 50% | 381 | 287 | 428 | 292 | 356 |
| 60% | 428 | 307 | 434 | 310 | 366 |
| 70% | 480 | 325 | 441 | 326 | 376 |
| 80% | 540 | 341 | 451 | 340 | 382 |
| 90% | — | 358 | 469 | 358 | 393 |
| D.P. | — | 390 | 491 | 384 | 410 |

| Description | Mid-Cont. gas oil | Mid-Cont. crude | Wrinkler crude | Mid-Cont. gas oil | Wrinkler gas oil naphtha blend | Naphtha-kero. blend |
|---|---|---|---|---|---|---|
| Sample no.[7] | 22 | 23 | 24 | 25 | 26 | 27 |
| °API | 35·5 | 37·3 | 26·6 | 36·9 | 32·9 | 47·8 |
| ASTM : | | | | | | |
| I.B.P. | 475 | 130 | 188 | 268 | 190 | 96 |
| 10% | 512 | 230 | 326 | 346 | 319 | 172 |
| 20% | 529 | 302 | 430 | 406 | 380 | 240 |
| 30% | 543 | 386 | 505 | 464 | 432 | 298 |
| 40% | 556 | 467 | 578 | 519 | 480 | 346 |
| 50% | 570 | 550 | 640 | 567 | 526 | 393 |
| 60% | 586 | 632 | 720 | 603 | 571 | 428 |
| 70% | 604 | 730 * | 805 * | 641 | 612 | 455 |
| 80% | 627 | 850 | 900 * | 691 | 647 | 481 |
| 90% | 663 | 1030 * | 1010 * | 746 | 692 | 516 |
| E.P. | 730 | 1350 † | 1110 † | 804 | 747 | 575 |
| EFV : | | | | | | |
| B.p. | 533 | 190 | 301 | 364 | 247 | 160 |
| 10% | 551 | 258 | 357 | 403 | 385 | 214 |
| 20% | 563 | 321 | 455 | 445 | 423 | 259 |
| 30% | 573 | 385 | 518 | 481 | 457 | 295 |
| 40% | 583 | 441 | 575 | 513 | 489 | 327 |
| 50% | 589 | 515 | 627 | 541 | 520 | 352 |
| 60% | 598 | 580 | 678 | 569 | 546 | 379 |
| 70% | 607 | 643 | 724 | 596 | 571 | 399 |
| 80% | 620 | — | — | 625 | 597 | 423 |
| 90% | 636 | — | — | 652 | 623 | 442 |
| D.P. | 665 | — | — | 683 | 650 | 464 |

* Corrected from vacuum distillation. † Extrapolated.

TABLE II—(*contd.*)

Sample No. 28: Std. Gaso.—60·0° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 132 | 157 | 75 |
| 10 | 155 | 166 | (98) |
| 20 | 186 | 187 | 153 |
| 50 | 267 | 236 | 257 |
| 70 | 312 | 260 | 317 |

Sample No. 29: 50% M-P O.H.—51·2° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 200 | (222) | 154 |
| 10 | 217 | (237) | 185 |
| 20 | 250 | 272 | 227 |
| 50 | 347 | 322 | 347 |
| 70 | 416 | (360) | 431 |

Sample No. 30: 80% M-P bottoms—34·1° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 297 | 334 | 262 |
| 10 | (327) | 382 | 302 |
| 20 | 380 | 430 | 367 |
| 50 | 563 | (580) | 610 |
| 70 | (710) | (678) | — |

Sample No. 34: Mexia Powell crude—35·9° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 229 | — | 193 |
| 10 | 270 | — | 234 |
| 20 | 343 | 354 | 314 |
| 50 | 560 | 525 | 555 |
| 70 | 700 | 638 | 722 |

Sample No. 35: Mid-Cont. crude—34·4° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 220 | — | 190 |
| 10 | 260 | (322) | 237 |
| 20 | 338 | 378 | 323 |
| 50 | 565 | 548 | 580 |
| 70 | 717 | 665 | (752) |

Sample No. 36: 50% col. O.H.—40·9° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 220 | 260 | 157 |
| 10 | 252 | 278 | 202 |
| 20 | 306 | 313 | 257 |
| 50 | 456 | 404 | 448 |
| 70 | 554 | 462 | 557 |

Sample No. 40: water white feed—42·1° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 373 | 394 | 320 |
| 10 | 379 | 401 | 337 |
| 20 | 390 | 410 | 366 |
| 50 | 428 | 433 | 426 |
| 70 | 466 | 451 | 476 |

Sample No. 41: water white bottoms—37·5° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 453 | 479 | 409 |
| 10 | 459 | 483 | 425 |
| 20 | 468 | 490 | 449 |
| 50 | 503 | 510 | 503 |
| 70 | 536 | 526 | 554 |

Sample No. 44: ranger crude—37·3° API [20]

| % | ASTM | Flash | T.B.P. | 38·0 | 37·8 |
|---|---|---|---|---|---|
| 5 | 235 | 285 | 175 | 173 | 162 |
| 10 | 270 | 308 | 226 | 216 | 213 |
| 20 | 330 | 353 | 313 | 294 | 302 |
| 50 | 543 | 499 | 545 | 544 | 538 |
| 70 | 690 | 630 | 705 | 738 | 717 |

Sample No. 46: Mid-Cont. crude—38·2° API [20]

| % | ASTM | Flash | T.B.P. | 38·2 | 38·6 |
|---|---|---|---|---|---|
| 5 | 176 | 247 | 143 | 138 | 142 |
| 10 | 212 | 275 | 196 | 194 | 198 |
| 20 | 289 | 351 | 282 | 283 | 282 |
| 50 | 524 | 536 | 582 | 551 | 547 |
| 70 | 708 | 653 | 693 | 757 | 744 |

Sample No. 31: Talang-Akar O.H.—45·7° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 279 | 307 | 222 |
| 10 | 296 | 320 | 248 |
| 20 | 321 | 335 | 282 |
| 50 | 400 | 375 | 394 |
| 70 | 456 | 402 | 466 |

Sample No. 32: 35% col. O.H.—46·9° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 202 | 231 | 143 |
| 10 | 227 | 248 | 182 |
| 20 | 267 | 275 | 223 |
| 50 | 386 | 337 | 361 |
| 70 | 450 | 375 | 455 |

Sample No. 33: 98% M-P bottoms—35·4° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 235 | — | 200 |
| 10 | 273 | — | 242 |
| 20 | 345 | 360 | 320 |
| 50 | 575 | 531 | (568) |
| 70 | 735 | 642 | (734) |

Sample No. 37: 70% col. bottoms—21·6° API [20]

| % | ASTM | Flash | T.B.P.C. |
|---|---|---|---|
| 5 | 450 | 521 | 388 |
| 10 | 488 | 550 | 453 |
| 20 | 567 | 606 | 535 |
| 50 | 792 | 780 | 780 |
| 70 | 963 | (898) | (953) |

Sample No. 38: Columbian crude—27·3° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 255 | 290 | 192 |
| 10 | 303 | 334 | 263 |
| 20 | 402 | 417 | 368 |
| 50 | 700 | 643 | 690 |
| 70 | (885) | 795 | 905 |

Sample No. 39: Esso gasoline—51·6° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 140 | 155 | — |
| 10 | 157 | 162 | 89 |
| 20 | 173 | 173 | 159 |
| 50 | 212 | 200 | 186 |
| 70 | 255 | 220 | 265 |

Sample No. 42: water white O.H.—46·4° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 352 | 362 | 300 |
| 10 | 356 | 366 | 315 |
| 20 | 361 | 369 | 338 |
| 50 | 377 | 376 | 377 |
| 70 | 390 | 380 | 401 |

Sample No. 43: unstripped gas oil—27·6° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 485 | 501 | 435 |
| 10 | 513 | 525 | 483 |
| 20 | 537 | 549 | 536 |
| 50 | 588 | 591 | 593 |
| 70 | 636 | 618 | 640 |

Sample No. 45: Mid-Cont. crude—35·3° API [20]

| % | ASTM | Flash | T.B.P. | 34·7 | 38·3 |
|---|---|---|---|---|---|
| 5 | 212 | 309 | 158 | — | 150 |
| 10 | 252 | 335 | 209 | 241 | 204 |
| 20 | 329 | 388 | 300 | 337 | 283 |
| 50 | 567 | 550 | 562 | 578 | 543 |
| 70 | 767 | 658 | 737 | 777 | 744 |

Sample No. 47: Mid-Cont. crude—37·1° API [20]

| % | ASTM | Flash | T.B.P. | 37·1 | 38·3 |
|---|---|---|---|---|---|
| 5 | 194 | 265 | 154 | 122 | 150 |
| 10 | 245 | 296 | 200 | 182 | 204 |
| 20 | 310 | 357 | 284 | 280 | 283 |
| 50 | 554 | 541 | 547 | 553 | 543 |
| 70 | 735 | 665 | 734 | 773 | 744 |

Sample No. 48: Colombian crude—26·8° API [20]

| % | ASTM | Flash | T.B.P. | 26·9 | 26·6 |
|---|---|---|---|---|---|
| 5 | 255 | 360 | 205 | 182 | 194 |
| 10 | 315 | 406 | 276 | 263 | 278 |
| 20 | 440 | 490 | 400 | 389 | 413 |
| 50 | 713 | 665 | 691 | 697 | 735 |
| 70 | 875 | 750 | 853 | 887 | 951 |

Sample No. 49: Kansas crude—40·8° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 176 | 250 | 155 |
| 10 | 212 | 269 | 199 |
| 20 | 266 | 307 | 262 |
| 50 | 475 | 442 | 475 |
| 70 | 651 | 544 | 636 |

Sample No. 51: Hendricks crude—32·5° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 221 | 299 | 180 |
| 10 | 266 | 326 | 235 |
| 20 | 338 | 382 | 312 |
| 50 | 545 | 533 | 536 |
| 70 | 715 | 627 | 729 |

Sample No. 54: Lobitos crude—36·8° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 205 | 230 | 185 |
| 10 | 224 | 256 | 214 |
| 20 | 269 | 308 | 250 |
| 50 | 464 | 454 | 438 |
| 70 | 662 | 546 | 622 |

Sample No. 56: Santa Fe Springs crude—32·4° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 212 | 251 | 184 |
| 10 | 252 | 290 | 221 |
| 20 | 315 | 364 | 300 |
| 50 | 578 | 565 | 562 |
| 70 | 764 | 698 | 748 |

Sample No. 58: Magnoland crude—28·2° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 411 | 450 | 334 |
| 10 | 446 | 460 | 404 |
| 20 | 490 | 483 | 486 |
| 50 | 559 | 553 | 581 |
| 70 | 638 | 599 | 665 |

Sample No. 50: Elwood crude—36·5° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 194 | 260 | 184 |
| 10 | 230 | 282 | 220 |
| 20 | 290 | 330 | 270 |
| 50 | 454 | 467 | 465 |
| 70 | 626 | 556 | 637 |

Sample No. 52: T.B.M. crude—41·1° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 172 | 261 | 182 |
| 10 | 212 | 296 | 215 |
| 20 | 280 | 360 | 283 |
| 50 | 491 | 530 | 507 |
| 70 | 658 | 632 | 686 |

Sample No. 55: Penn. crude—43·1° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 212 | 311 | 183 |
| 10 | 250 | 345 | 226 |
| 20 | 310 | 388 | 300 |
| 50 | 531 | 520 | 524 |
| 70 | 671 | 610 | 675 |

Sample No. 57: Luling crude—34·9° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 324 | 397 | 278 |
| 10 | 361 | 421 | 323 |
| 20 | 421 | 456 | 403 |
| 50 | 603 | 563 | 591 |
| 70 | 725 | 635 | 717 |

Sample No. 59: treated P.D.—51·8° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 135 | 145 | — |
| 10 | 165 | 165 | — |
| 20 | 213 | 199 | — |
| 50 | 313 | 273 | — |
| 70 | 374 | 318 | — |

Sample No. 60: crude—29·5° API [20]

| % | ASTM | Flash | T.B.P. |
|---|---|---|---|
| 5 | 135 | 145 | — |
| 10 | 165 | 165 | — |
| 20 | 213 | 199 | — |
| 50 | 313 | 273 | — |
| 70 | 374 | 318 | — |

| Description | East Texas heavy naphtha | Mid-Cont. heavy naphtha | Crude heavy naphtha | | Crude light naphtha | |
|---|---|---|---|---|---|---|
| Sample no. | 61 [18] | 62 [18] | 63 [8] | | 64 [8] | |
| °API | 50·4 | 51·8 | 49·3 | | 64·8 | |
| ASTM: | | | | | | |
| I.B.P., °F | 224 | 250 | 250 | | 111 | |
| 5% recovered | 254 | 281 | — | | — | |
| 10% recovered | 263 | 288 | 291 | | 156 | |
| 20% recovered | 273 | 295 | 320 | | 177 | |
| 30% recovered | 282 | 303 | 340 | | 192 | |
| 40% recovered | 294 | 310 | 354 | | 207 | |
| 50% recovered | 303 | 316 | 370 | | 219 | |
| 60% recovered | 312 | 323 | 381 | | 232 | |
| 70% recovered | 322 | 330 | 397 | | 248 | |
| 80% recovered | 334 | 340 | 413 | | 264 | |
| 90% recovered | 353 | 356 | 437 | | 293 | |
| 95% recovered | 373 | 380 | — | | — | |
| E.P. | 399 | 422 | 477 | | 361 | |
| Residue, % | 1·2 | 1·0 | — | | — | |
| Loss, % | 0·8 | 1·0 | 0·5 | | 1·0 | |
| EPV: | | | % Vap. | °F | % Vap. | °F |
| I.B.P. | 283 | 275 | — | — | — | — |
| 10% vaporized | 295 | 286 | 3·7 | 329 | 5·38 | 173 |
| 20% vaporized | 303 | 293 | 14·9 | 344 | 24·7 | 181 |
| 30% vaporized | 309 | 298 | 45·1 | 365 | 51·0 | 199 |
| 40% vaporized | 314 | 304 | 59·3 | 374 | 54·5 | 204 |
| 50% vaporized | 318 | 309 | 85·0 | 396 | 78·2 | 218 |
| 60% vaporized | 322 | 313 | 91·0 | 403 | 86·6 | 229 |
| 70% vaporized | 325 | 317 | 97·7 | 413 | 90·6 | 235 |
| 80% vaporized | 330 | 322 | — | — | — | — |
| 85% vaporized | 333 | 324 | — | — | — | — |

TABLE II—(*contd.*)

| Description | 70% West Texas, 30% Mid-Cont. reduced crude | | 30% West Texas, 70% Mid-Cont. reduced crude | | Mid-Cont. reduced crude | |
|---|---|---|---|---|---|---|
| Sample no.[37] | 67 | | 68 | | 69 | |
| °API | 20·5 | | 23·6 | | 23·5 | |
| ASTM : | | | | | | |
| I.B.P. | — | | — | | — | |
| 5% | 519 | | 519 | | 502 | |
| 10% | 585 | | 574 | | 557 | |
| 20% | 651 | | 619 | | 608 | |
| 30% | 691 | | 658 | | 654 | |
| 40% | 739 | | 691 | | 672 | |
| 50% | 797 | | 735 | | 701 | |
| 60% | 850 | | 790 | | 742 | |
| 70% | 916 | | 858 | | 800 | |
| 72% | 930 | | — | | — | |
| 79% | — | | 907 | | — | |
| 80% | — | | — | | 877 | |
| 85% | — | | — | | 924 | |
| EFV : | % Vap. | °F | % Vap. | °F | % Vap. | °F |
| | 6·9 | 640 | 11·8 | 640 | 3·8 | 600 |
| | 17·4 | 690 | 28·9 | 690 | 13·9 | 640 |
| | 26·2 | 720 | 39·9 | 730 | 29·2 | 680 |
| | 39·4 | 760 | 66·8 | 760 | 60·6 | 730 |
| | 57·2 | 800 | 71·6 | 800 | 78·1 | 800 |

| Description | West Texas | Oklahoma | Oklahoma |
|---|---|---|---|
| Sample no.[24] | 71 | 74 | 75 |
| °API | 22·3 | 24·4 | 24·2 |
| ASTM : | | | |
| I.B.P. | 598 | 693 | 660 |
| 5% condensed | 666 | 718 | 715 |
| 10% condensed | 701 | 739 | 731 |
| 20% condensed | 768 | 769 | 770 |
| 30% condensed | 825 | 806 | 810 |
| 40% condensed | 883 | 842 | 861 |
| 50% condensed | 938 | 897 | 911 |
| 60% condensed | 993 | 945 | 970 |
| 70% condensed | 1053 | 1013 | 1043 |
| 80% condensed | — | 1077 | 1102 |
| 90% condensed | — | — | — |
| 95% condensed | — | — | — |
| EFV : | | | |
| I.B.P. | — | — | — |
| 30% condensed | 845 | — | — |
| 40% condensed | 873 | — | — |
| 50% condensed | 908 | 890 | — |
| 60% condensed | 951 | 925 | 945 |
| 70% condensed | 1010 | 978 | 990 |
| 80% condensed | 1100 | 1042 | 1048 |
| 90% condensed | — | 1130 | 1132 |
| 95% condensed | — | 1178 | 1185 |

| Sample no.[38] | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 |
|---|---|---|---|---|---|---|---|---|
| Crude no. | 1 | 2 | 4 | 5 | 7 | 8 | 9 | 10 |
| Gravity | 34·8 | 37·0 | 34·1 | 32·1 | 33·1 | 31·0 | 42·4 | 24·5 |
| | | | | ASTM, °F | | | | |
| Distillation % off : | | | | | | | | |
| IBP | 145 | 160 | 172 | 205 | 146 | 200 | 112 | 174 |
| 10 | 310 | 282 | 298 | 350 | 250 | 325 | 208 | 383 |
| 20 | 400 | 360 | 390 | 434 | 333 | 402 | 258 | 471 |
| 30 | 471 | 426 | 451 | 477 | 400 | 461 | 324 | 525 |
| 40 | 528 | 483 | 492 | 506 | 461 | 515 | 397 | 563 |
| 50 | 582 | 531 | 533 | 538 | 505 | 570 | 477 | 611 |
| 60 | 640 | 563 | 582 | 562 | 560 | 629 | 560 | 678 |
| 70 | 700 | 641 | 647 | 597 | 619 | 699 | 651 | 751 |
| 80 | 765 | 732 | 729 | 650 | 695 | 787 | 780 | 828 |
| 90 | — | 847 | 839 | 717 | 780 | — | — | — |
| | Experimental EFV (Othmer still), °F | | | | | | | |
| Distillation % off : | | | | | | | | |
| IBP | — | — | — | — | — | 250 | 130 | — |
| 10 | — | — | — | — | — | 409 | 234 | 455 |
| 20 | — | — | — | — | — | 445 | 278 | 501 |
| 30 | — | — | — | — | — | 482 | 328 | 537 |
| 40 | — | — | — | — | — | 507 | 370 | 574 |
| 50 | — | — | — | — | — | — | 430 | 601 |
| 60 | — | — | — | — | — | 581 | 482 | 657 |
| 70 | — | — | — | — | — | 614 | 550 | 708 |
| 75 | — | — | — | — | — | 642 | — | — |
| 80 | — | — | — | — | — | 692 | 655 | 773 |
| 85 | — | — | — | — | — | — | 690 | 816 |
| 90 | — | — | — | — | — | 750 | — | — |
| | Experimental EFV (modified UOP Cont. still) % flashed | | | | | | | |
| Distillation % off : | | | | | | | | |
| 420 | 22·4 | 30·0 | 20·8 | 12·1 | 2·6 | 15·4 | — | 8·2 |
| 500 | 39·5 | 53·6 | 41·1 | 41·4 | 17·9 | 40·2 | — | 25·7 |
| 550 | — | — | 58·6 | 60·0 | 35·2 | 48·5 | — | 40·6 |
| 600 | 60·5 | — | 69·3 | 77·0 | 54·8 | 63·4 | — | 51·2 |
| 650 | 65·7 | — | 79·6 | 85·0 | 75·6 | 73·3 | — | 59·2 |

| | Crude | Crude | Vac. over. | Gas oil | Gasoline |
|---|---|---|---|---|---|
| Sample no.[4] | 86 | 88 | 90 | 91 | 92 |
| °API | 45·1 | 37·4 | 27·0 | 22·8 (D158) | 56·0 |
| ASTM (D86) : * | | | | | |
| 0% | 100 | 128 | 330 | 488 | 104 |
| 5% | 162 | 195 | 398 | 510 | 144 |
| 10% | 191 | 234 | 436 | 515 | 172 |
| 20% | 242 | 286 | 474 | 525 | 222 |
| 30% | 284 | 344 | 495 | 534 | 264 |
| 40% | 336 | 407 | 507 | 544 | 293 |
| 50% | 404 | 461 | 519 | 555 | 309 |
| 60% | 475 | 510 | 530 | 566 | 317 |
| 70% | 547 | 565 | 540 | 578 | 323 |
| 80% | — | — | 553 | 595 | 330 |
| 90% | — | — | 568 | — | 337 |
| EP | — | — | 602 | — | 369 |
| EFV laboratory : † | | | | | |
| 0% | 190 | 204 | 437 | — | 169 |
| 10% | 222 | 273 | 475 | — | 206 |
| 20% | 258 | 324 | 492 | 544 | 233 |
| 30% | 295 | 367 | 501 | 555 | 253 |
| 40% | 334 | 404 | 509 | 564 | 266 |
| 50% | 376 | 444 | 516 | 570 | 277 |
| 60% | 417 | 488 | 524 | 575 | 286 |
| 70% | 463 | 534 | 532 | 579 | 295 |
| 80% | 511 | 582 | 538 | 584 | 303 |
| 90% | 566 | 632 | 546 | — | 310 |
| EP | — | — | — | — | 316 |

* Recovered temperature. † Atmospheric pressure.

is for gas, oil, and similar products. Its reproducibility is ±9° F at the end point, and ±6° F over 6 ml at the other points. The method for the determination of equilibrium flash vaporization has not yet been standardized. However, it is not expected that any significant deviation may result from the diversified sources of the data.

## CORRELATION

After careful analyses and studies of existing correlations and attempts at many arrangements in arriving at an improved correlation, a method which is a modification of Edmister and Pollock is developed giving the least deviation from experimental data. This consists of an improved method in estimating the 50 per cent EFV point, followed by the same method of incremental slopes of Edmister and Pollock.[7] In Fig 1 the difference of the 50 per cent point between ASTM and EFV curves is plotted versus the 50 per cent point of ASTM distillation curves, using as parameter the slope of a straight line connecting the 10 per cent and 70 per cent point of ASTM distillation curves. This plot is based upon the statistical average of sixty-five sets of data selected for the development of correlation. The other slopes have been tried, including that of 10–30 per cent slope used by Edmister and Pollock.[7] The 10–70 per cent slope of the ASTM curve is used as the parameter in the correlation because the resulting correlation gives a better fit to the experimental data. With the correlation represented by Fig 1 the 50 per cent point of the EFV curve can be obtained from the data of ASTM distillation.

A further refinement in estimating the 50 per cent EFV point can be made with a correlation represented by Fig 2, which shows the difference of 50 per cent EFV between the estimated value from Fig 1 and the more refined value is again plotted versus 10–70 per cent slope of ASTM distillation curve using

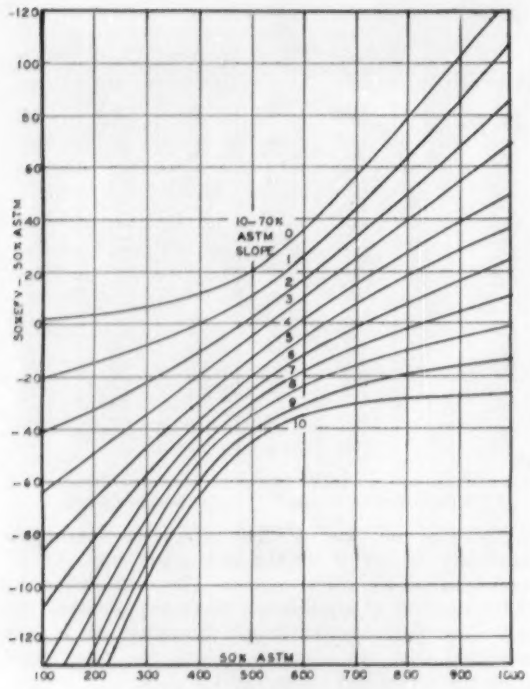


FIG 1

RELATION BETWEEN 50 PER CENT EFV AND 50 CENT CENT ASTM POINT

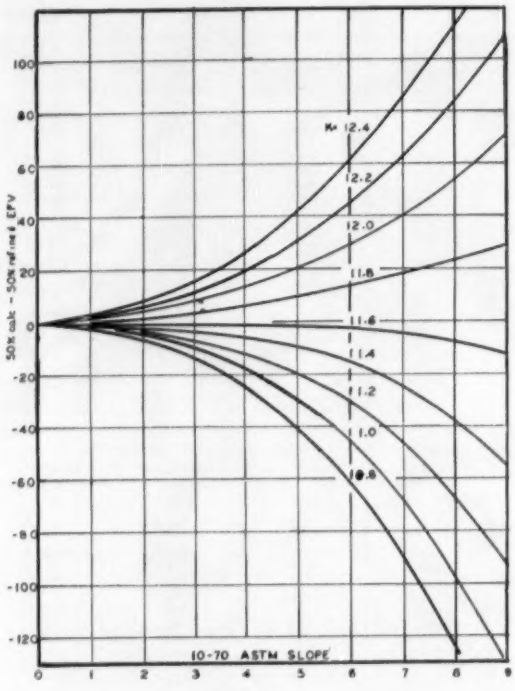


FIG 2

FURTHER CORRECTION FOR 50 PER CENT ON EFV CURVE

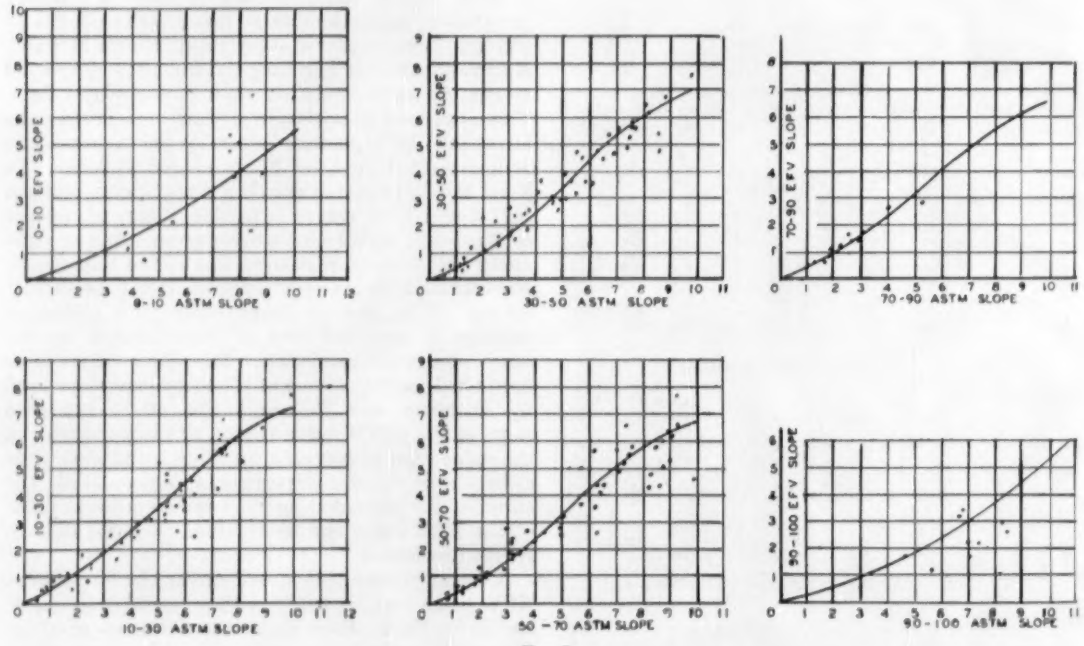


FIG 3

COMPARISON OF EXPERIMENTAL DATA WITH THE SLOPE CURVES OF EDMISTER *ET AL.*

Points = experimental data. Curve = Edmister's correlation.

characterization factor as parameter. The characterization factor, K,[11, 35] used in the correlation, is obtained from API gravity and ASTM distillation data with the aid of a chart given by Maxwell.[13, 36] In the correlation represented by Fig 2, the characterization factor varies from 10·8 to 12·4 and the correction varies in a wide range −120° to +110° F. The characterization factor is introduced here to account for the difference in aromaticity.

With the refined 50 per cent point established on the EFV curve, the other points along the curve can be obtained by the same method proposed by Edmister and Pollock,[7] who gave the curves relating the slope of EFV with that of ASTM. Altogether six curves are given for the slope in the ranges of 0–10, 10–30, 30–50, 50–70, 70–90, and 90–100 per cent. These curves are checked with selected sets of data. In Fig 3 the experimental data are located along with the curves given by Edmister and Pollock.[7] Although there appears some scattering, the curves are a fair representation of statistical average. The agreement between the curves and experimental data is especially good in the middle range of distillation, *i.e.* 10–30, 30–50, 50–70, 70–90 per cent, where the experimental data are more accurate. For this reason Edmister and Pollock's slope curves are used in the modified correlation and the refined 50 per cent point on EFV is located.

The application of the correlation can be illustrated by estimating the curve of equilibrium flash vaporization of a mixed base crude having the following ASTM distillation data [31] :

ASTM Distillation, ° F

| API Gravity | Initial | 5% | 10% | 20% | 30% |
|---|---|---|---|---|---|
| 37·9° | 150 | 211 | 272 | 333 | 389 |

| 40% | 50% | 60% | 70% | 80% | EBP | % Recovery |
|---|---|---|---|---|---|---|
| 445 | 497 | 542 | 596 | 688 | 777 | 88 |

## CALCULATION

Assume 1 per cent loss, the ASTM distillation data are corrected to give :

| Volume % off | Temp, ° F |
|---|---|
| 0 | 134 |
| 10 | 264 |
| 30 | 384 |
| 50 | 490 |
| 70 | 590 |

10–70 per cent ASTM slope =

$$\frac{590 - 264}{60} = 5{\cdot}5^\circ \text{ F per cent}$$

Volumetric average b.p. = 490° F
Mean av. b.p. [13] = 424 ° F
Characterization Factor [13] = 11·45
From Fig 1 at 50 per cent ASTM of 490° F and 10–70 per cent slope of 5·5° F per cent
50 per cent EFV point = 490 − 35 = 465° F
From Fig 2 at UOP K = 11·45
50 per cent EFV corrected = 465 − (−9) = 474° F

With this 50 per cent EFV of 474 ° F the calculation of other EFV points are done in the following table :

| Volume % off | ASTM Temp ° F | ASTM Temp difference, ° F | ASTM Slope, ° F/% | EFV Temp difference, ° F | EFV Temp, ° F | EFV Slope, ° F/% |
|---|---|---|---|---|---|---|
| 0 | 134 | | | | | 234 |
| 10 | 264 | 130 | 13 | 7 | 77 | 311 |
| 30 | 384 | 120 | 6 | 4·5 | 90 | 401 |
| 50 | 490 | 106 | 5·3 | 3·65 | 73 | 474 |
| 70 | 590 | 100 | 5·0 | 3·3 | 66 | 540 |

The same ASTM distillation data are also treated by Maxwell's and Edmister and Pollock's methods to obtain the atmospheric equilibrium flash vaporiza-

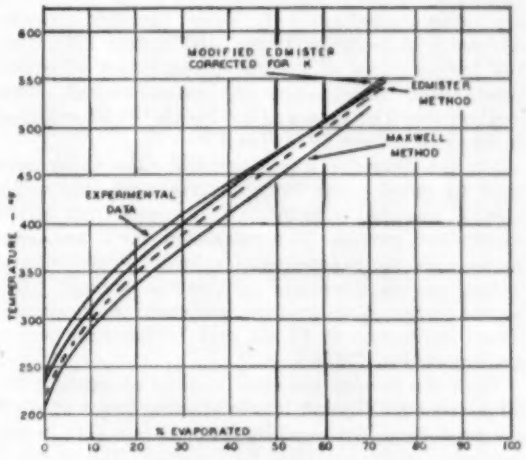


Fig 4

COMPARISON OF VARIOUS METHODS OF EQUILIBRIUM FLASH CURVE CALCULATION

Table III

*Comparison of Equilibrium Flash Curves as Calculated by Various Methods*

| % Evap. | Experimental | Maxwell | Edmister | Modified Edmister corrected for " K " |
|---|---|---|---|---|
| IBP | 242 | 231 | 217 (est.) | 227 (est.) |
| 10 | 325 | 303 | 300 | 310 |
| 30 | 411 | 384 | 390 | 400 |
| 50 | 475 | 453 | 464 | 474 |
| 70 | 535 | 508 | 530 | 540 |

tion data. These calculated values, together with experimental data of equilibrium flash vaporization, are given in Table III, and are graphically compared in Fig 4. It can be seen that the present modifica-

tion of Edmister and Pollock's method gives better agreement with experimental data.

## DISCUSSION OF RESULTS

In estimating EFV curve from ASTM distillation data, Maxwell's method consists of several steps. First draw a straight line through the 10 per cent and 70 per cent points on a plot where ASTM distillation temperatures are plotted versus volume percentage of distillation. This line is referred to as "Distillation Reference Line." [13] The next step is to find the temperature corresponding to the 50 per cent point on the "Distillation Reference Line" (DRL). The "Flash Reference Line" (FRL) is then located by obtaining 50 per cent and its slope from the charts developed by Maxwell.[13] The temperature differences between the flash equilibrium vaporization curve and FRL are found at different volume percentages of vaporization by multiplying the temperature difference between ASTM and DRL by a factor. The factors at different percentages are fixed values and are graphically given.[13] With the temperature difference between DRL and ASTM, and FRL line, the temperatures at different percentages of equilibrium flash vaporization can be calculated. This method was first proposed by Packie [19] and modified to its present form by Maxwell.[13]

For the sixty-five sets of selected data which were used to develop the present correlation, Maxwell's method was used to estimate EFV curves from ASTM distillation curves. The calculated EFV are compared with the experimental values. Four kinds of deviations are reported: arithmetic average, algebraic average, mean average, and standard deviation. These deviations at 10, 30, and 70 per cent points are reported in Table I.

With the present proposed method of locating the 50 per cent EFV point, it is interesting to see whether the procedure developed by Maxwell can give better prediction of the complete EFV curve. The so-called modified Maxwell's method, without the use of characterization factor, is operated as follows:

Use Fig 1 to estimate the 50 per cent EFV point from ASTM distillation data. Find the temperature difference between EFV and FRL by the same procedure of Maxwell. With the temperature difference between EFV and FRL obtained, the 50 per cent FRL point can be readily calculated from the 50 per cent EFV. With all the rest of the procedure identical to that of Maxwell, the complete EFV can be estimated. The calculated EFV are compared with experimental data for the sixty-five sets of data used for developing the correlation. The deviation at 10 per cent point is $\pm 15{\cdot}60°$ F in arithmetic average; $-3{\cdot}62°$ F in algebraic average; $16{\cdot}45°$ F in mean average, and $27{\cdot}1°$ F in standard deviation. The corresponding deviations at 30 per cent point are $\pm 15{\cdot}56$ °F, $-6{\cdot}01°$ F, $15{\cdot}5°$ F, and $24{\cdot}0°$ F. At 70 per cent point the corresponding deviations are $\pm 15{\cdot}39°$ F, $+0{\cdot}72°$ F, $15{\cdot}35°$ F, and $22{\cdot}3°$ F.

If further correction upon 50 per cent EFV point by the characterization factor is made, the Maxwell's procedure gives better results, as indicated by the deviations given under modified Maxwell's method, with the use of characterization factor, in Table I. The same sixty-five sets of experimental data were also treated by Edmister and Pollock's procedure with their original charts. By omitting the correction for characterization factor, the same data were treated by Edmister and Pollock's method after the location of 50 per cent EFV point by Fig 1. This is so-called modified Edmister's method, without the use of characterization factor. The results of comparison with experimental data in terms of four kinds of deviations are all given at 10, 30, and 70 per cent point in Table I.

Okamoto and van Winkle [17] presented a new correlation to estimate the EFV curve from ASTM distillation. The calculated EFV was compared with the present sixty-five sets of data. The deviations at 70 per cent are $\pm 46{\cdot}3°$ F in arithmetic average; $+44{\cdot}5°$ F in algebraic average; 28° F in mean deviation, and $35{\cdot}3°$ F in standard deviation. The corresponding deviations at 50 per cent point are $\pm 26{\cdot}2°$, $+19°$, $20{\cdot}9°$, and $27{\cdot}1°$ F. In Table I also are the deviations at the 10 per cent, and 30 per cent points. It appears that Okamoto and van Winkle's correlation give the highest deviation from experimental data as far as atmospheric pressure is concerned.

Many other methods were attempted with varying degrees of success. Included in the study was the effect of slope ratio which was defined as the ratio of the slope at 10–30 per cent to that of 40–70 per cent ASTM distillation curves. Those mixtures containing predominantly light components would have a slope ratio less than unity, whereas the mixtures with heavy components would have a slope ratio greater than unity. This variable, however, could not find its way into the correlation. Relationships similar to those developed for the estimation of 50 per cent EFV points were tried out at the other points on the flash curve. Correlations were obtained for all the other points, but none of these gave results in better agreement with experimental data than the correlation presented in this paper. The effect of the characterization factor was also studied at other points on the flash curve. No correlation could be obtained. The other variables, which were investigated with varying degree of success, include average molecular weight, volumetric average boiling point, and the ratio of the 10–30 ASTM slope to the 60–70 ASTM slope.[29]

It is assumed that the characterization factor would have as much an effect on any point of the flash curve as it does on the 50 per cent point. As it does not appear to benefit the 70 per cent points, some doubt is cast on the validity of the correction by the characterization factor at the 50 per cent point. Also, the 50 per cent point correction due to the characterization factor may be a unique one in that the original error was back-plotted against one of the

original variables (slope) on the characterization factor correction graph; and the final error was reduced, but not through the effect of the characterization factor. On the other hand, if the error could be reduced in such a fashion, it should have reduced the error at the 10 per cent point and the 70 per cent point.

Most uncertainties in predicting EFV values by empirical methods exist in the ends of the curves. Also, those materials with wide boiling ranges show greater errors than those with narrow boiling ranges. It is believed that the increased slopes are the cause of these uncertainties. There are areas where the temperature is increasing at a relatively rapid pace, while lag in reading exists in the thermometer. Whenever the temperature is rising rapidly, the observer is likely to make errors of observation. Consequently, the experimental error is quite reasonably responsible for this uncertainty.

## ACKNOWLEDGMENT

Grateful acknowledgement is made to the following companies who have generously contributed data for this paper: Standard Oil Development Co., California Research Corpn, Pan American Oil Co., Phillips Petroleum Co., Socony-Vacuum Oil Co., Sun Oil Co., The Texas Co., Universal Oil Products, and Sinclair Research Laboratories.

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# OBITUARY

## MAURICE ALBION OCKENDEN

THE death of Maurice Albion Ockenden at the age of seventy-nine on 2 December 1954, removes a respected and popular figure of prominence in London business circles who accepted his share of civic life responsibilities. As the direct descendant of the founder of one who established an engineering firm which dealt mainly with water problems along the South Coast of England, he, through the medium of a London office, extended the firm's spheres of activities to overseas; and the drilling and pumping plant they manufactured acquired a merited reputation in many of Britain's Colonies and Dependencies, as well as foreign countries. Prior to this Ockenden had spent some time in the U.S.A., where he learnt much about American drilling methods and business customs.

As far back as 1910 he was induced to transfer his allegiance to the world-famous establishment of the Oil Well Supply Company of Pittsburg and Oil City, Pennsylvania, U.S.A., and in the capacity of London Manager employed his talents in salesmanship of oilfield equipment such as British engineering firms were then unable to supply. With the aid of able colleagues, including the late Ashley Carter and Cecil T. Longcroft, he built up a fine organization in London. Although he made strenuous efforts to induce his principals to manufacture oilfield equipment in Britain, he failed, notwithstanding that some negotiations he conducted almost ended in success. During his service with this great Corporation he paid visits to the U.S.A. and to many European oilfields.

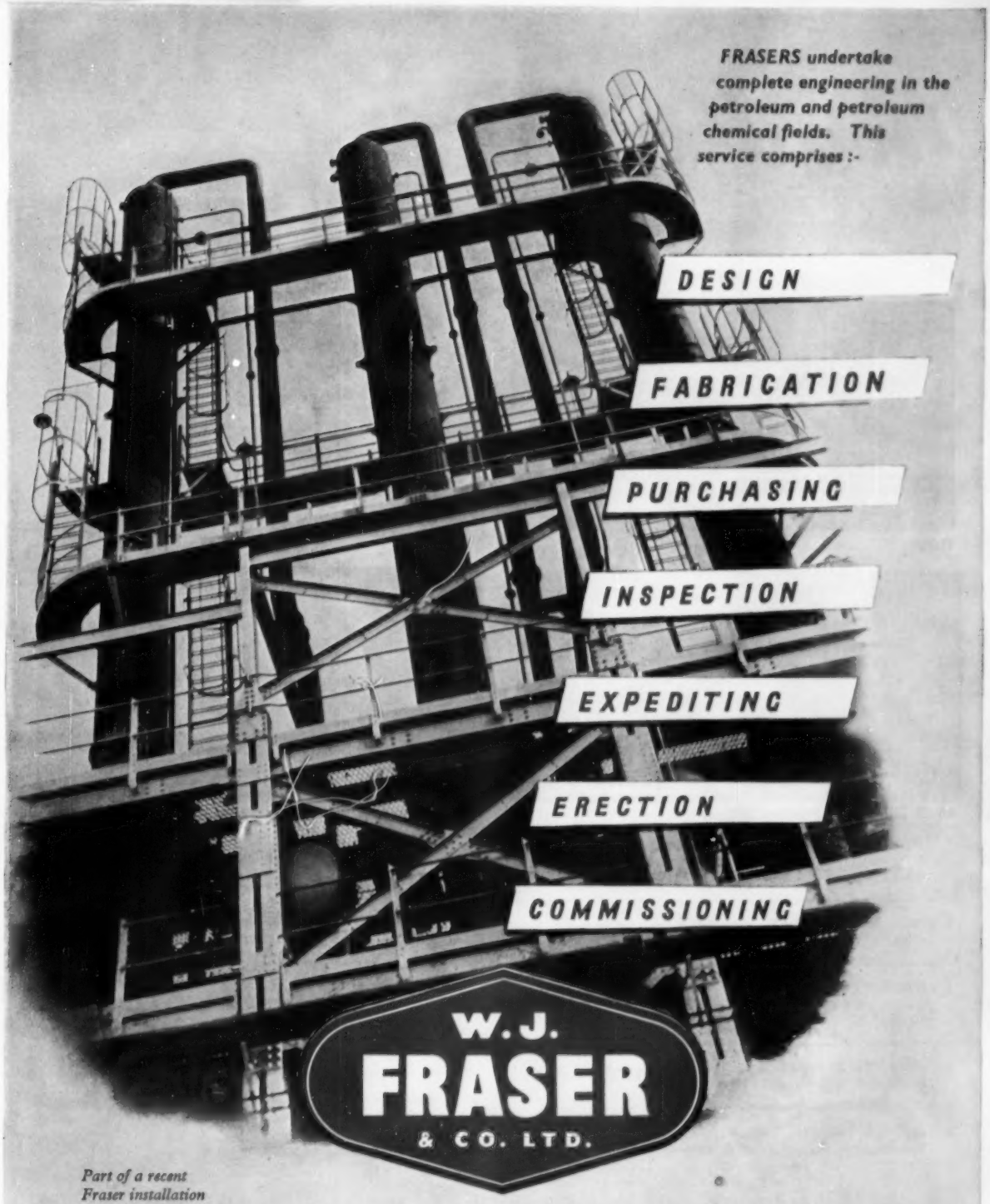
The lamented death in 1926 of that remarkable and able American head of the O.W.S., Louis Sands, led to changes which ended with the control of the concern being transferred to the United States Steel Corporation of the Carnegie Group; and this event decided his severance with the Company and a return to his old firm as Director and Controller in London. By making this decision he sustained his relations with City friends and with civic life in which he participated. His duties entailed commercial relations with most of the leading oil companies prospecting or developing oil properties in many parts of the world.

From 1925 until a few months prior to his death Ockenden was on the Council of the London Chamber of Commerce and served on the Commercial Education Committee. He was a freeman of the City of London and Liveryman of the Guild of Turners. As a Fellow of the Geological Society and a member of the Geologists Association, he was a frequent attendant at meetings and field excursions. He was a Founder Member of the Institute of Petroleum and duly made a Fellow when that status was created. His extensive experience with water supply problems that arose from his firm's operations in England and elsewhere led to his advice being frequently sought by public bodies and Institutions. He was since 1913 a member of the Institution of Mechanical Engineers and was also a member of Institute of Structural Engineers.

For many years he was a member of the Gresham Club in the City and later of the Chemical Club in Whitehall. He will best be remembered by the sympathetic hearing he always gave to all who sought information or advice, or were in search of occupation, for despite his activity, none was refused a hearing when they called at his office in Victoria Street. In addition to other commitments he was a director of Pre-piling Surveys and of Associated Drilling and Supply Company, of London.

He took a lively interest in social life at Sanderstead, where he had resided for many years. He leaves a widow, Amy, and a family of three gifted daughters, all of whom have established for themselves a high reputation in their respective spheres of activity.

A. BEEBY THOMPSON

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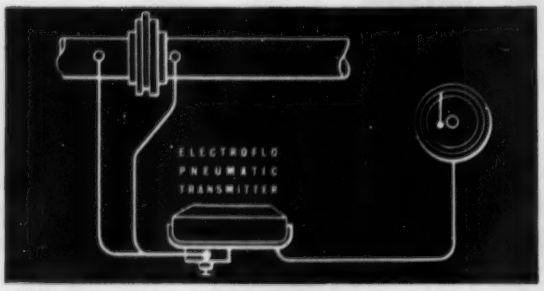


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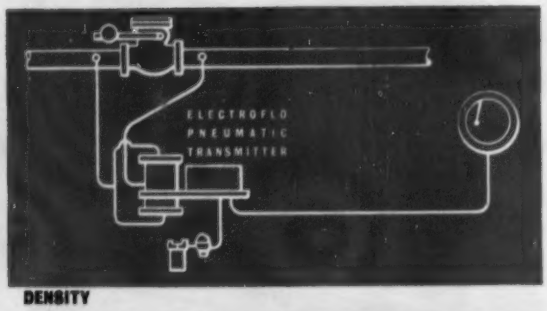


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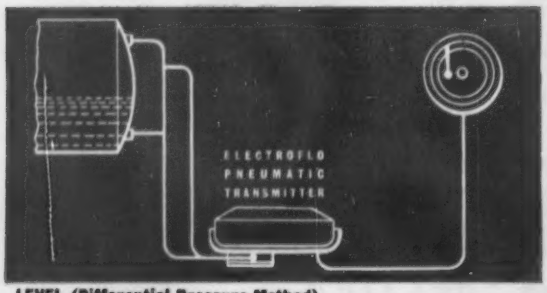


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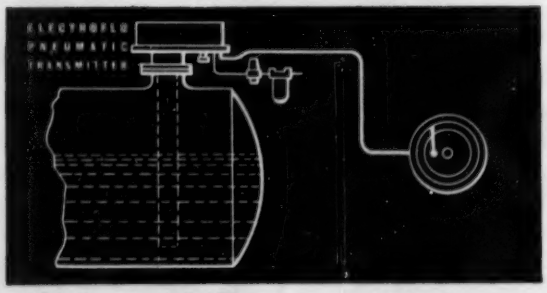


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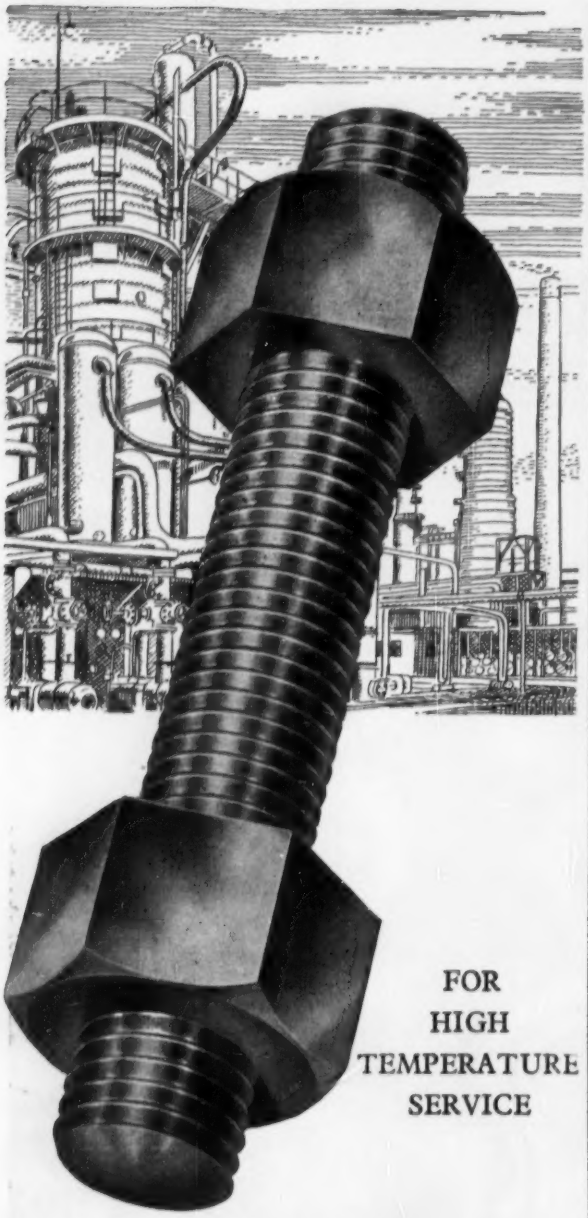

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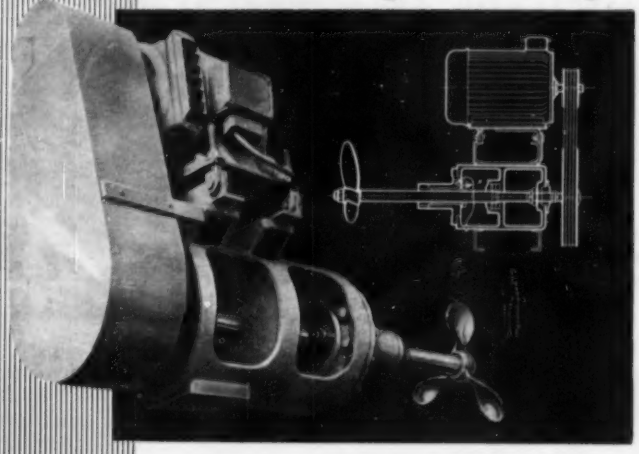

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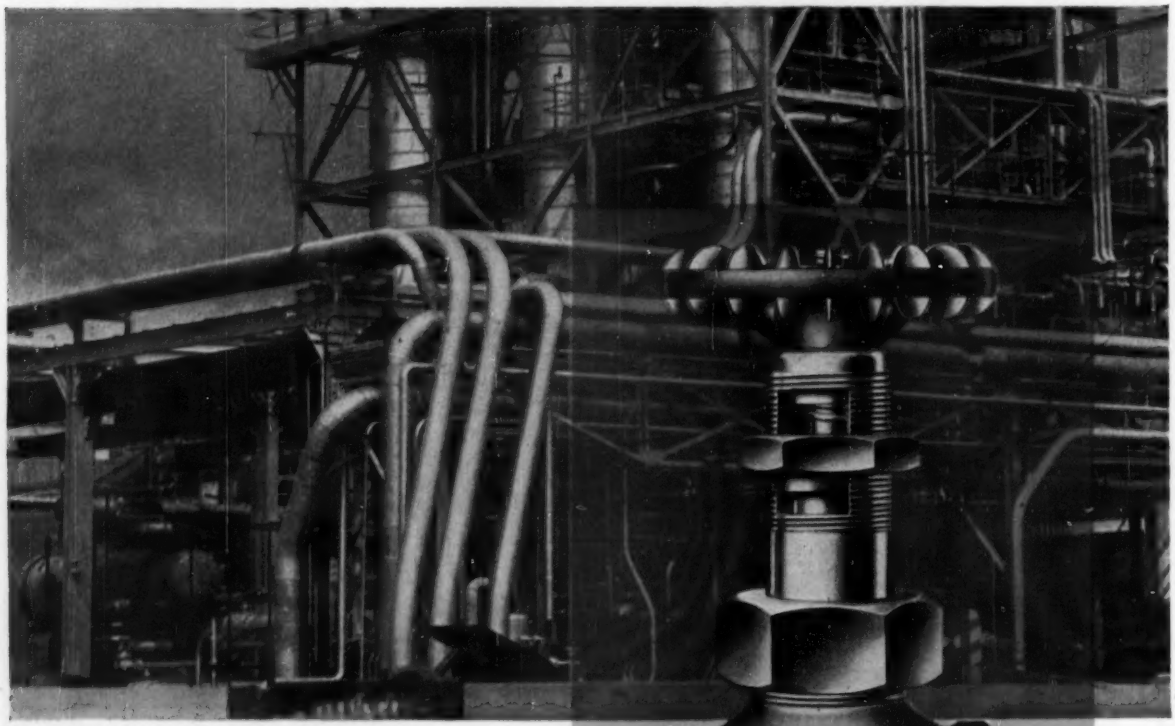

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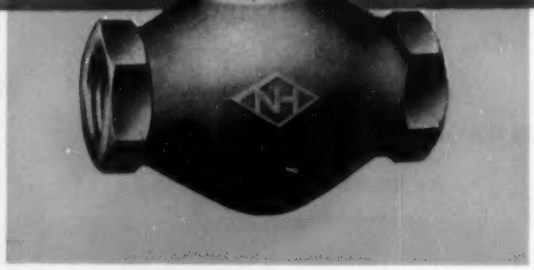

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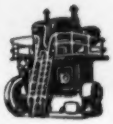

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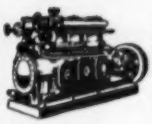

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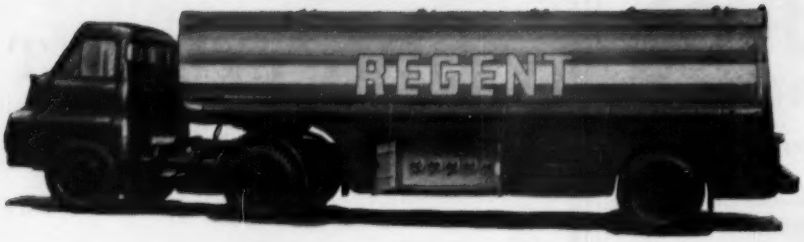


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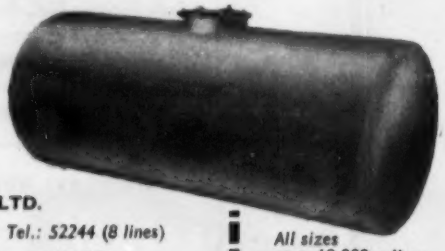

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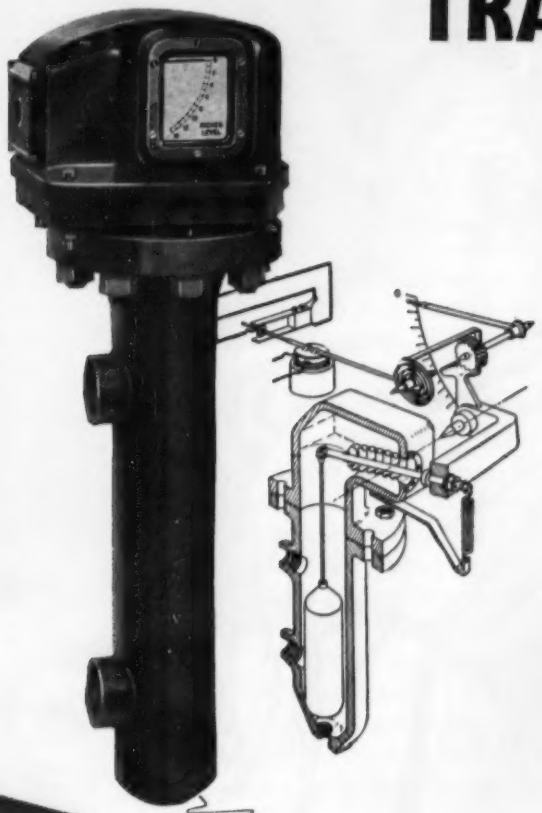

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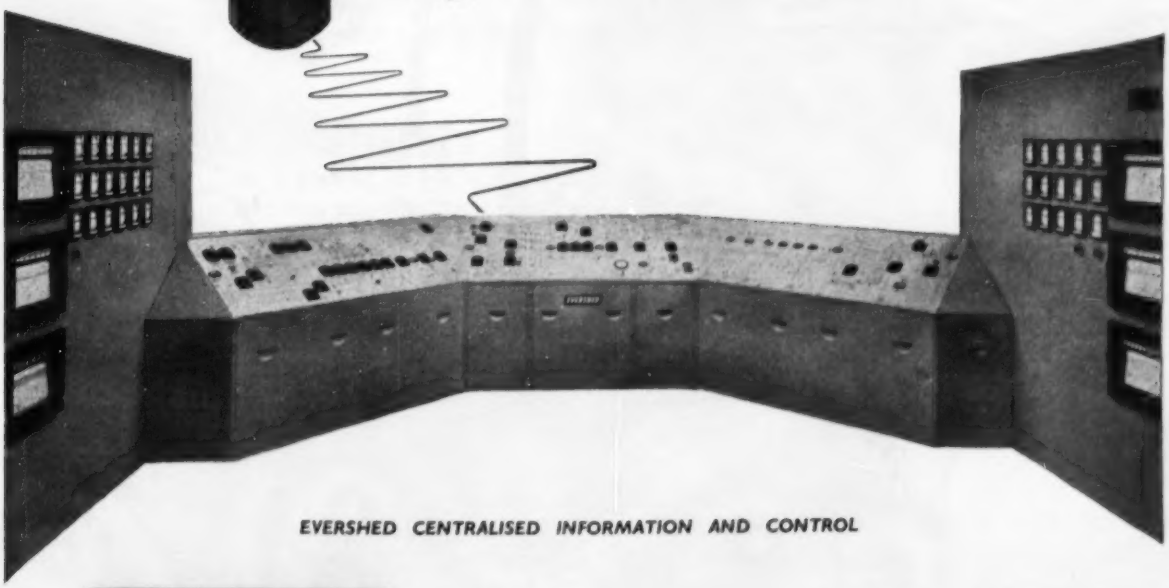

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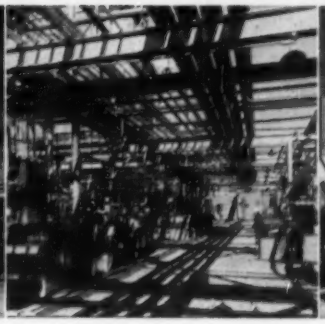

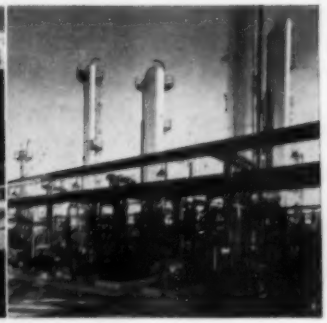

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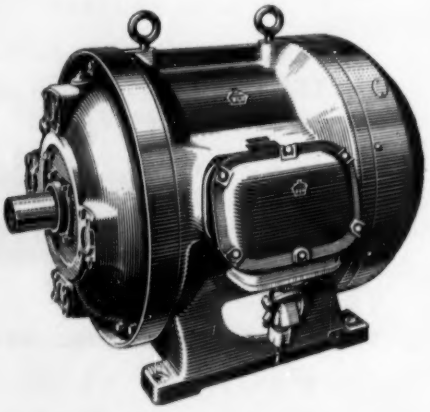

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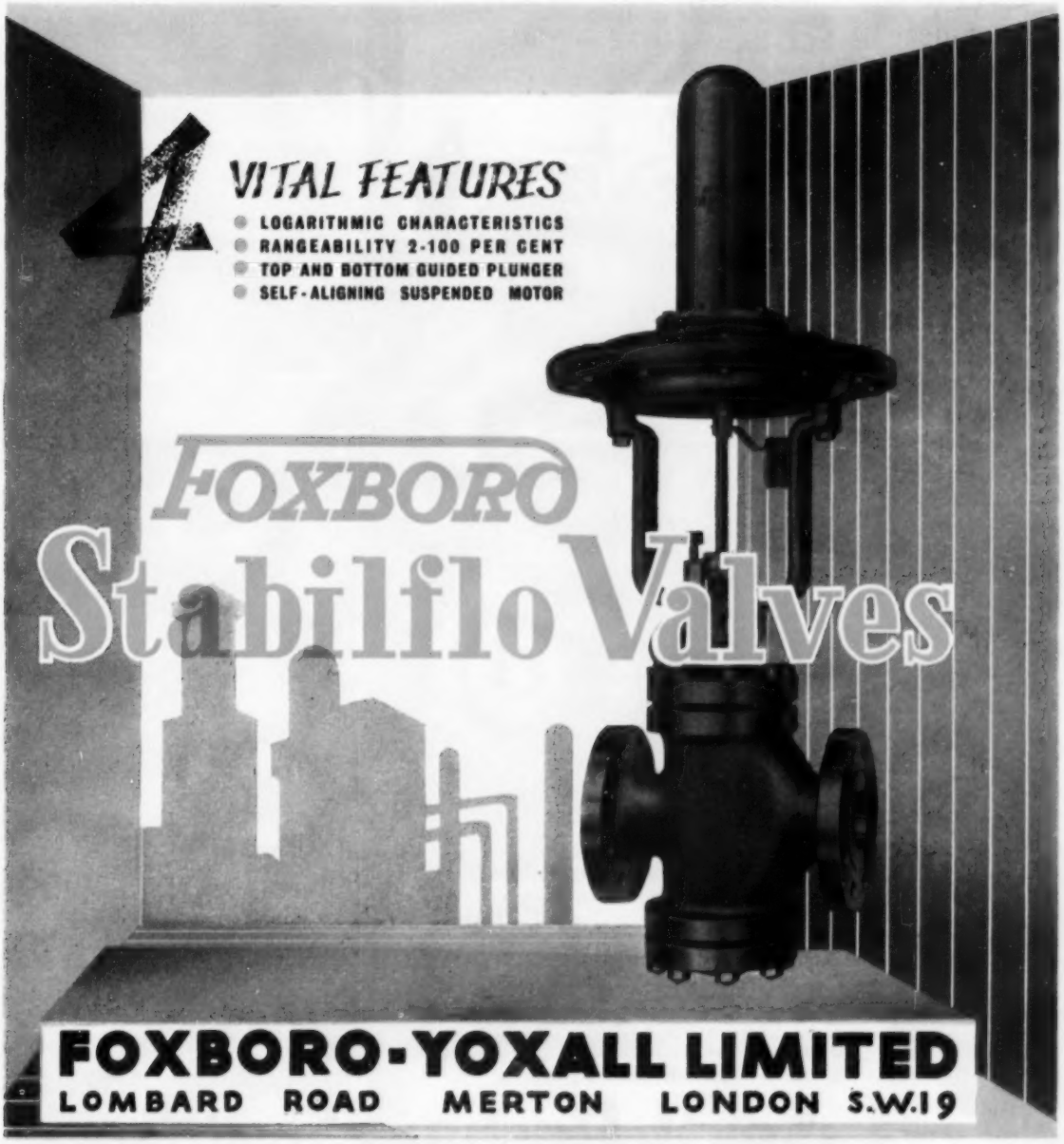
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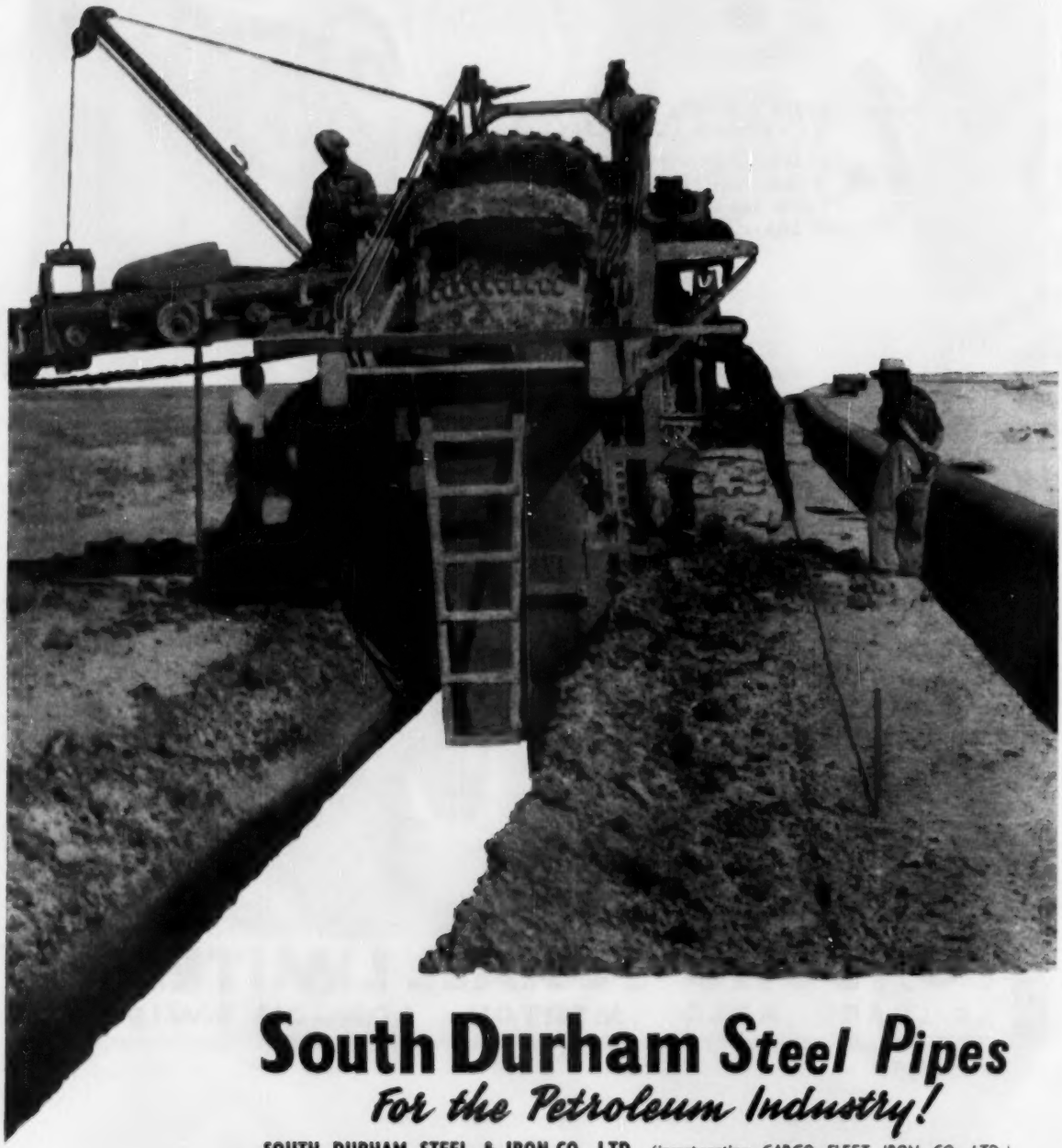

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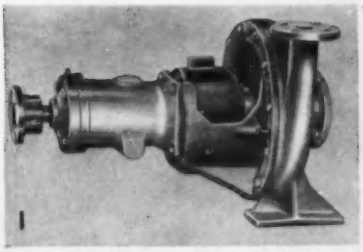


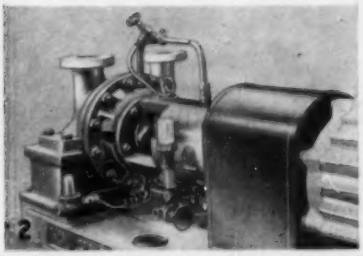


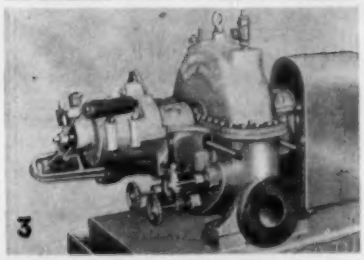


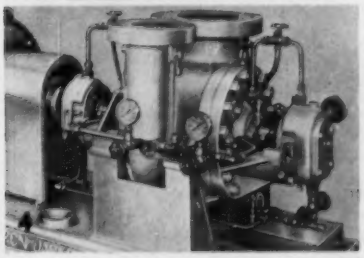


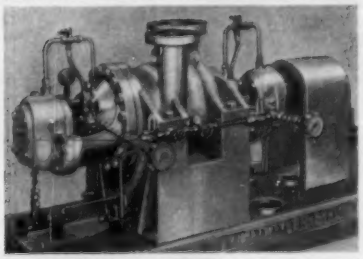

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